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SANTA CLARA VALLEY WATER DISTRICT

LLAGAS GROUNDWATER BASIN NITRATE STUDY

SAMPLE ANALYSIS

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SANTA CLARA VALLEY WATER DISTRICT

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LLAGAS GROUNDWATER BASIN NITRATE STUDY

CONTRACT NO. 1-053-250-0

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I. EXECUTIVE SUMMARY

Communities in the southern portion of Santa Clara County rely solely on groundwater from Llagas Basin for their water supply. Over the years, groundwater from municipal and private water supply wells has been found to contain concentrations of nitrate greater than those allowed by federal safe drinking water standards. The Santa Clara Valley Water (District) is responsible for managing the groundwater basin to ensure its viability as a long term potable water supply. The District, as well as other local agencies, is concerned that the elevated nitrate concentrations in Llagas Basin may impact the utilization of the groundwater basin as the sole water supply. The Llagas Groundwater Basin Nitrate Study is exploring nitrate exposure prevention and source reduction alternatives and will recommend a specific nitrate management plan for the Llagas Groundwater Basin.

The present Maximum Contaminant Level (MCL) for nitrate in drinking water is 45 milligrams per liter (mg/l), as promulgated by the United States Environmental Protection Agency (USEPA). Higher concentrations of nitrate have been known to cause adverse health effects in infants.

Measures are being taken to ensure that drinking water standards for nitrate are being met. Affected municipal water supply wells are either no longer used or the groundwater from them is blended with groundwater from other wells containing lower concentrations of nitrate. Also, some of the private wells are using wellhead treatment systems to remove nitrates from the water.

The study is being performed in the following phases: (1) review of historic nitrate data, (2) identification of categories of nitrate sources, (3) field sample collection, (4) evaluation of groundwater analytical results, and (5) development of a Nitrate Management Plan. During the first phase of work, the District evaluated historical nitrate concentrations in the groundwater of the study area. These evaluations are found in the study report ``Nitrate Data Review'' dated August 1993. During the second phase of the study, the District identified sources of nitrate contamination in the study area and reported the results in the report ``Nitrate Source Area Identification'' dated December 1994. The report ``Sample Point Selection'' dated December 1994 contains a summary of the methodology for selecting nitrate sample collection points and a map showing the locations of the sample collection points that were selected. During the phase of the study described in this report, the District collected and analyzed groundwater quality data. Subsequent phases of the study will focus on developing alternative strategies for reducing nitrate concentrations in order to continue providing a water supply that meets safe drinking water standards to the people of Llagas Basin. The overall nitrate study is scheduled for completion in February of 1996.

A Technical Advisory Committee (TAC), including members of the community, has been assisting the District throughout the study, but is expected to provide the most input during the development of the Nitrate Management Plan.

LLAGAS BASIN GROUNDWATER FLOW

Llagas Basin has two hydrogeologic regions. One region is referred to as the forebay region, where rainfall and artificially recharged water percolates through the ground directly into the underlying aquifer. The forebay region is located in the northern part of Llagas Basin. The second region is known as the confined region and is located in the southern part of Llagas Basin.

In the confined region a thick clay layer, known as an aquitard, separates the deeper water producing aquifers from shallow aquifers. Groundwater on top of this clay layer is primarily from rainfall, whereas groundwater flowing underneath the clay layer primarily originates in the forebay region. There is some vertical interconnection between these aquifers through old wells that may be screened in both shallow and deep aquifers. Other potential vertical connections between the aquifers include rootholes and geologic discontinuities.

The direction of groundwater flow in Llagas Basin is primarily south towards the Pajaro River. Due to the variable characteristics of the basin, the depth to ground water below ground surface differs throughout the basin but normally ranges from between 10 to 70 feet below ground surface.

FORMATION AND TRANSPORT OF NITRATES

Nitrate is produced when compounds which contain nitrogen (human and livestock waste, agricultural fertilizers, etc.) are introduced into the environment where they are transformed into nitrate in the soil via mineralization and nitrification. Mineralization is the process of organic nitrogen compounds being transformed into inorganic nitrogen compounds such as ammonium salts. Nitrification is the process of bacteria transforming those inorganic nitrogen compounds into nitrates. Except for certain chemical reactions that form minor amounts of nitrate from oxides of nitrogen in the atmosphere, this biological nitrification of nitrogenous compounds is the sole source of nitrate in the environment.

Once nitrogen containing compounds have been transformed into nitrate through mineralization and nitrification, the nitrate can dissolve in water percolating through the soil and be transported downward into groundwater aquifers. As stated in the ``Identification and Evaluation of Methods for Determining Sources of Nitrate Contamination in Groundwater: Guidance Manual'' by Rolston, et al., (Guidance Manual), it can take anywhere between 10 to 100 years for nitrate to travel through the vadose zone and reach groundwater. The vertical migration of nitrate is dependent on the amount of water infiltrating the soil, the soil type, and the depth to groundwater.

Nitrates found in groundwater today may have originated from previous sources which are not reflected in current land uses because it may take a considerable amount of time for nitrate to be transported to groundwater. Though some practices which generate nitrate have been discontinued, groundwater quality may still be affected over time due to the transport of dissolved nitrates in water percolating through the soil. The time required for the movement of nitrate from the ground surface to groundwater depends on local conditions related to precipitation, transport in soil, plant nitrate uptake, and other processes. The nitrates which are found in groundwater today may have been released from the soil over several years or decades. Thus, soil containing high nitrate concentrations may still be considered a source of nitrate contamination to groundwater even though the practices that originally released the nitrogen to the soil have been discontinued.

OBJECTIVES OF SAMPLE COLLECTION

The ``Sample Point Selection'' report dated December 1994 discusses in detail why and how wells were selected for sampling during this study. In summary, wells were selected in order to (1) continue analysis of nitrate trends in six wells in the study area and (2) monitor groundwater quality in the vicinity of known nitrogen source areas. Also, two wells screened only in the shallowest groundwater zone were selected to provide depth-specific data for that zone, and two wells located outside of the valley floor of the study area were selected to provide ``background''[1] water quality data. Rainwater samples were also collected to provide information on the nitrogen content of rainwater.

In addition to nitrate, the following analytes were included in the sampling program: nitrite, dissolved oxygen, $\delta^{15}N$ (stable nitrogen isotope ratio), $\delta^{18}O$ (stable oxygen isotope ratio), Total Kjeldahl Nitrogen, ammonia, chloride, and coliform. These analytes were chosen with the expectation that they could help identify nitrate sources in the study area.

Two deviations were made from the contract during this phase of the study. First, the contract for this study required sample collection from only 25 wells in the study area. However, samples were collected from a total of 28 wells so that additional data could be collected for the purposes described above. Second, the contract required that samples be collected during January and July of 1993. These dates were altered in order to accommodate a revised schedule, which extended the completion date of the study from June of 1994 to February of 1996.

LIMITATIONS OF SAMPLE ANALYSIS

With the data collected and the degree of analysis performed thus far, definitive conclusions regarding the specific sources of nitrate in the well water sampled as part of this study cannot be drawn. Although additional analytes such as $\delta^{15}N$ were used in our program, the fact that additional work such as vadose zone sampling and detailed hydrogeologic evaluation in the vicinity of each source was not performed precludes us from tracing nitrates in groundwater back to specific source areas or facilities (Rolston, et al., 1994a and b). Nitrates present in a well may be due to a mix from two or more sources. The relationship of these sources to contaminated wells may not be readily apparent from merely viewing regional maps and groundwater direction, as preferential migratory pathways and irregularities in local groundwater flow may exist, and can cause a distant nitrate source to actually become a significant source. Therefore, with a known nitrate concentration and a known $\delta^{15}N$ value from a specific well, for instance, one is still unable to conclusively identify the specific contaminant source. This is especially true in the study area, which features complex subsurface geology, and multiple types and a high number of nitrate sources.

There are additional reasons not to attempt to identify nitrate sources with isotopic signatures alone (Rolston, et al., 1994). Denitrification can increase a nitrogen's $\delta^{15}N$ value, and may lead to erroneous interpretation of isotope results if not fully considered. The reported $\delta^{15}N$ ranges for soil organic nitrogen and fertilizer are also very similar, and distinguishing between these two sources solely on the basis of isotope values would be impossible. However, certain suspected types of sources of nitrate can be ruled out based on isotope values alone; other factors, such as historical land use and climate, can be used to correlate source types.

SUMMARY OF SAMPLING RESULTS

The sampling results from this phase of the study are generally consistent with the historic results presented in the ``Nitrate Data Review'' report dated August 1993.

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[1] These wells are considered ``background'' because their location precludes them from being affected by the dense concentration of major anthropogenic sources on the valley floor identified in the source identification phase of the study. Additionally, high recharge rates may be observed in the wells since they are located near creeks.

First, the results confirmed that nitrates still exist in the groundwater of Llagas Basin. Twenty-five percent of the wells sampled produced water with nitrate concentrations greater than 45 mg/l, the federally mandated Maximum Contaminant Level (MCL) for drinking water; almost 50 percent contained between 25 and 45 mg/l, and the remainder contained nitrate concentrations below 25 mg/l.

Second, results from the six wells resampled for trend analysis confirmed the presence of nitrates in groundwater from these wells. All of the results fell within the ranges of historical concentration data. However, samples from two of the wells contained concentrations lower than would be expected if historical results were extrapolated into the future using a straight-line trend analysis. Nitrate concentrations in one of the six wells were the highest concentrations found in that well, historically.

Performing a detailed geologic evaluation is essential in order to identify the specific source(s) of nitrate in a particular well (Rolston 1994a and b, et al.). Such an evaluation is beyond the scope of this study. Therefore, conclusions could not be drawn regarding which specific source contributed to nitrate found in a well. However, some general conclusions were able to be drawn about the data and its relationship to source identification. For example, both ``background'' wells produced samples with very low nitrate concentrations, indicating that the valley floor of the study area is where the significant source(s) of nitrates in groundwater can be found. Also, distance between a nitrate source and a contaminated well appeared to have little effect on the amount of nitrates found in a well. Some wells located in the immediate vicinity of known nitrate sources contained water with low nitrate concentrations, while others produced water with nitrate concentrations in excess of MCLs.

The data collected during this phase of the nitrate study will aid in the development of the Nitrate Management Plan. Conclusions drawn from the areal and vertical distribution of nitrates, nitrate trends, nitrates and source areas, and supplementary analytes will help us when developing nitrate management recommendations. Our sample collection has also pointed out which aspects of nitrate source identification require additional field investigation.

II. INTRODUCTION

The Llagas Groundwater Basin Nitrate Study is being conducted by the Santa Clara Valley Water District (District) with partial funding from the State Water Resources Control Board (SWRCB) because the District has observed a general trend of increasing nitrate concentrations in Llagas Basin groundwater. The purpose of this phase of the study is to collect and analyze groundwater quality data from Llagas Basin. Subsequent phases of the study will focus on recommending an implementation plan for the prevention, control, and monitoring of nitrates.

The southern portion of Santa Clara County, including the cities of Morgan Hill and Gilroy, and the area of San Martin, depends solely on the groundwater from Llagas Basin for its drinking and irrigation water supply. Figure 1 shows the location of the Llagas Basin study area. Current land use distribution in the Llagas Basin area is as follows: about 40 percent agricultural area, 25 percent Urban Service area, 20 percent Rural Residential area, and 5 percent parks and open space. The remaining 10 percent of the land has various land use classifications such as Public Transportation, Educational/Institutional, and Public Facilities. These percentages are based on Santa Clara County's 1991 ``Land Use Plan'' and have been verified by Santa Clara County Department of Planning and Development staff (personal communication, 1993).

NITRATE HEALTH EFFECTS

The present Maximum Contaminant Level (MCL) for nitrate in drinking water is 45 milligrams per liter (mg/l), as promulgated by the United States Environmental Protection Agency (USEPA). Drinking water supplies with concentrations exceeding this level are considered out of compliance, and require treatment and/or alternative supplies.

In Llagas Basin, numerous wells have exceeded the federal MCL of 45 mg/l. As outlined in the District's ``Nitrate Data Review'' report, one third of the wells that have been sampled in Llagas Basin contained nitrate in concentrations above the 45 mg/l MCL. Nitrate concentrations exceeded 100 mg/l at several locations. Elevated nitrate concentrations are a concern because of the susceptibility of infants to methemoglobinemia (blue baby syndrome) resulting from exposures to higher levels of nitrates in water. In addition, research is being done to determine whether excess nitrates in food and drinking water might also have long term carcinogenic (tendency to cause cancer) or teratogenic (tendency to cause fetal malformations) effects on exposed populations.

FORMATION AND TRANSPORT OF NITRATES

Nitrate is produced when compounds which contain nitrogen (human and livestock waste, agricultural fertilizers, etc.) are introduced into the environment and transformed into nitrate in the soil via mineralization and nitrification. Mineralization is the process of organic nitrogen compounds being transformed into inorganic nitrogen compounds such as ammonium salts. Nitrification is the process of bacteria transforming those inorganic nitrogen compounds into nitrates. Except for certain chemical reactions that form minor amounts of nitrate from oxides of nitrogen in the atmosphere, this biological nitrification of nitrogenous compounds is the sole source of nitrate in the environment.

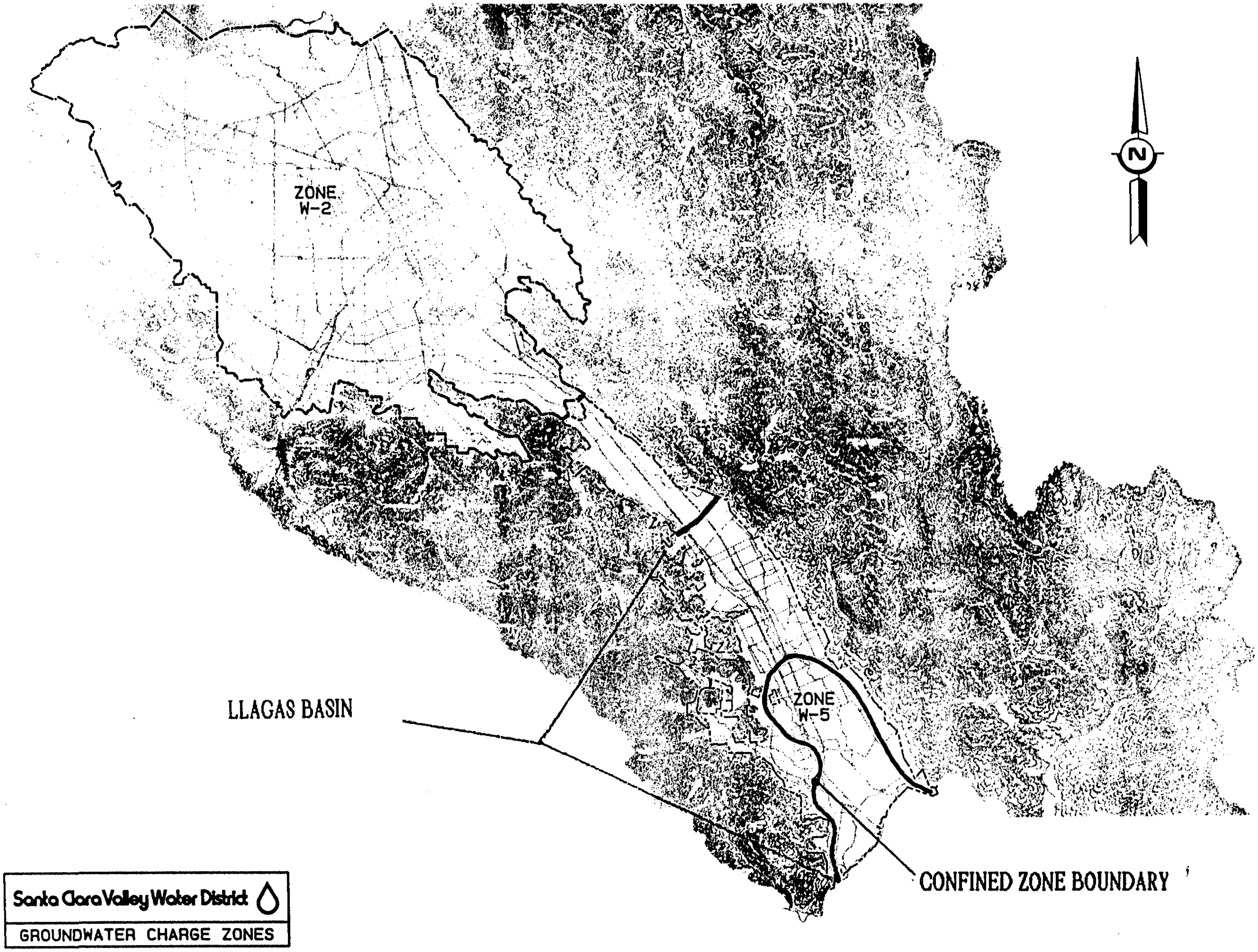

FIGURE 1: SANTA CLARA VALLEY AND LLAGAS BASIN

Nitrogen is introduced into the environment from a variety of sources. In a 1976 study conducted by Miller and Smith for the San Joaquin River Basin in the San Joaquin Valley, California, seven primary nitrogen sources were identified. The sources included municipal wastes, industrial wastes, livestock manures, agricultural fertilizers, waterborne nitrogen (nitrogen bearing water entering the study area via stream and groundwater flow), nitrogen fixation (reduction of nitrogen gas to ammonia and organic nitrogen by various microorganisms), and precipitation. Results from the study reported nitrogen contributions from the various sources as follows: municipal wastes—2 percent, industrial wastes—4 percent, livestock manures—18 percent, agricultural fertilizers—43 percent, waterborne nitrogen—13 percent, nitrogen fixation—18 percent, and precipitation—2 percent. Because we find many of the same land use types in Llagas Basin, we have found that many of the same sources of nitrogen are significant contributors to the Llagas Basin. It should be noted, however, that Llagas Basin is more urbanized than the San Joaquin Basin and therefore the relative amounts of nitrogen introduced by municipal wastes (i.e. septic tank and wastewater treatment plant effluent) is expected to be higher.

Once nitrogen containing compounds have been transformed into nitrate through mineralization and nitrification, the nitrate can dissolve in water percolating through the soil and be transported downward into groundwater aquifers. It can take a considerable amount of time for nitrate to reach groundwater because the vertical migration of nitrate is dependent on the amount of water infiltrating the soil, the soil type, and the depth to groundwater. After nitrates reach groundwater they typically move in the direction of groundwater flow.

OVERALL STUDY TASKS AND STATUS

The study started on October 1, 1991, and is scheduled to be completed on February 29, 1996. The agreement between the SWRCB and the District for the study consists of the following eleven tasks:

- Manage and Administer Project. This is an ongoing task.
- Conduct Public Participation Meetings. One out of two meetings has been held.
- Develop Quality Assurance Project Plan. This task has been completed.
- Review Historical Nitrate Data. This task has been completed.
- Identify Nitrate Source Categories. This task has been completed.
- Select Sample Collection Points. This task has been completed.
- Collect and Analyze Samples and Data[2].
- Review Legislative Mechanisms and Management Plan to Control the Nitrate Problem.
- Prepare Implementation, Institutional, and Financial Plans.
- Prepare Draft Final Report.
- Prepare Final Report.

Four of the tasks have already been completed. These tasks include developing a Quality Assurance Project Plan; completing the ``Nitrate Data Review'' report, which summarized and evaluated nitrate data from previous studies; completing the ``Nitrate Source Area Identification'' report which identified and attempted to quantify the sources of nitrate present in Llagas Basin; and completing the ``Sample Point Selection'' report which summarized the methodology for selecting nitrate sample collection points and presented the selected wells. The remaining tasks include developing a plan for the prevention, reduction, and monitoring of nitrates. A review of existing and potential legislative mechanisms for controlling nitrates is being performed with input from a Technical Advisory Committee (TAC). The TAC is composed of representatives from the SWRCB, the Central Coast Regional Water Quality Control Board (CCRWQCB), the cities of Gilroy and Morgan Hill, and the County of Santa Clara.

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[2] Present status of study.

SAMPLE COLLECTION RESULTS

This portion of the Nitrate Study presents and discusses the data gathered during the sample collection phase of the study. The methodology used to select the sampling locations is presented in the December 1994 ``Sample Point Selection'' report. Data collected during December 1993 and February/March 1994 confirmed the presence of nitrates in the groundwater of Llagas Basin, provided more information for nitrate trend analysis, and allowed us to make limited conclusions regarding the sources of nitrate in the study area.

LIMITATIONS OF SAMPLE ANALYSIS

This portion of the Nitrate Study involved obtaining, tabulating, and analyzing current groundwater quality data from 28 wells in the study area. Each well was sampled twice for nitrates; a variety of other analytes such as nitrates, ammonia, Total Kjeldahl Nitrogen (TKN), dissolved oxygen, chloride, $\delta^{15}N$, and $\delta^{18}O$ were also incorporated into our sampling program. Additional analytes were incorporated into the sampling program, to provide more data for possible nitrate source identification. Overall, the data enabled us to draw conclusions about nitrate occurrence, distribution, and trends in the study area.

With the data collected and the degree of analysis performed thus far, definitive conclusions regarding the specific sources of nitrate in the well water sampled as part of this study cannot be drawn. Although additional analytes such as $\delta^{15}N$ were used in our program, the fact that additional work such as vadose zone sampling and detailed hydrogeologic evaluation in the vicinity of each source was not performed precludes us from tracing nitrates in groundwater back to specific source areas or facilities (Rolston, et al., 1994a and b). Nitrates present in a well may be due to a mix of two or more sources. The relationship of these sources to contaminated wells may not be readily apparent from merely viewing regional maps and groundwater direction, as preferential migratory pathways and irregularities in local groundwater flow may exist, and can cause a distant nitrate source to actually become a significant source. Therefore, with a known nitrate concentration and a known $\delta^{15}N$ value from a specific well, for instance, one is still unable to conclusively identify the specific contaminant source. This is especially true in the study area, which features complex subsurface geology, and multiple types and a high number of nitrate sources.

There are additional reasons not to attempt to identify nitrate sources with isotopic signatures alone (Rolston, et al., 1994). Denitrification can increase a nitrogen's $\delta^{15}N$ value, and may lead to erroneous interpretation of isotope results if not fully considered. The reported $\delta^{15}N$ ranges for soil organic nitrogen and fertilizer are also very similar, and distinguishing between these two sources solely on the basis of isotope values would be impossible. However, certain suspected types of sources of nitrate can be ruled out based on isotope values alone; other factors, such as historical land use and climate, can be used to correlate source types.

III. GEOLOGY AND HYDROGEOLOGY OF LLAGAS BASIN

The geologic history of Llagas Basin has resulted in a complex hydrogeologic system consisting of confined and unconfined aquifers. As shown in Figure 1, Llagas Basin continues southeasterly from the southern end of Coyote Valley at the interconnecting topographic divide to the southern boundary of the County at the Pajaro River. The bulk of the alluvial materials washed into the basin is alluvial fan materials from Coyote Creek splaying southward from the topographic divide. Other major sources of alluvial fill material that comprise the basin are from Llagas Creek and Uvas Creek from the Santa Cruz Mountains which bound the west side of the basin. Small alluvial fans from small ephemeral drainage occur along both elevated lateral edges of the basin. As shown in Figure 2, the depth of alluvial fill and the underlying Santa Clara formation varies from about 500 feet at the northern divide to greater than 1,000 feet at its southern end. The Purissima Formation which underlies the alluvium and the Santa Clara Formation is, in part, water bearing in neighboring counties, but is not tapped here.

In general, the basin is divided into three hydrographic units. The northern portion of the basin and the elevated lateral edges of the basin constitute the forebay and the southern flat interior portion is divided into upper and lower aquifer zones (similar to Santa Clara Valley Basin).

The forebay comprises mostly aquifer materials with discontinuous aquitards, is unconfined, and is the principle basin recharge zone. Recharge is from subsurface inflow from Coyote Valley where a groundwater mound occurs beneath the topographic divide, from deep percolation of streams, principally along Llagas Creek north of Rucker Avenue, and from Uvas Creek west of U.S. Highway 101. Minor amounts of recharge can also be attributed to rainfall, irrigation returns, and from the subsurface flow from nonwater-bearing formations that laterally bind the basin. Within the forebay, groundwater generally flows from the topographic divide southeasterly down the basin toward the flat south central part of the basin.

Confining conditions which create both upper and lower aquifer zones occur in the flat southern interior portion of the basin and continue southerly past the County line into the Hollister Basin. The separation between the upper and lower aquifers is formed by a continuous regional aquitard that occurs at varying depths from about 20 to 100 feet, and extends from approximately Rucker Avenue to the south basin boundary. The thickness of this major aquitard varies from about 40 to 100 feet. Both upper and lower zones are stratified with aquifers and aquitards.

Groundwater in the upper aquifer zone is unconfined in the uppermost aquifer and confined or partially confined in deeper aquifers. The depth to groundwater in this zone is usually shallow and generally flows southeasterly, to the Pajaro River. Recharge to the upper aquifer zone is from surface sources and from subsurface flows from the forebay.

Numerous individual aquifers occur in the lower aquifer zone. Groundwater in these aquifers is confined and generally flows to the southeast except where the regional gradient is interrupted by pumping troughs. Subsurface flow from the forebay recharges these aquifers. From the mid-1800s, wells tapping the southern portion of this zone, south of Old Gilroy, were flowing artesian wells (Clark, 1924). With a greater amount of pumping in more recent times in proportion to growing water demands, the artesian pressures have declined and now only a few of the wells in the southernmost portion of the basin flow under pressure and are only on a seasonal basis.

In Llagas Basin most of the waters are pumped from the forebay and lower aquifer zones, though many of the wells in the flat southern interior portion of the basin pump from both upper and lower aquifer zones.[3]

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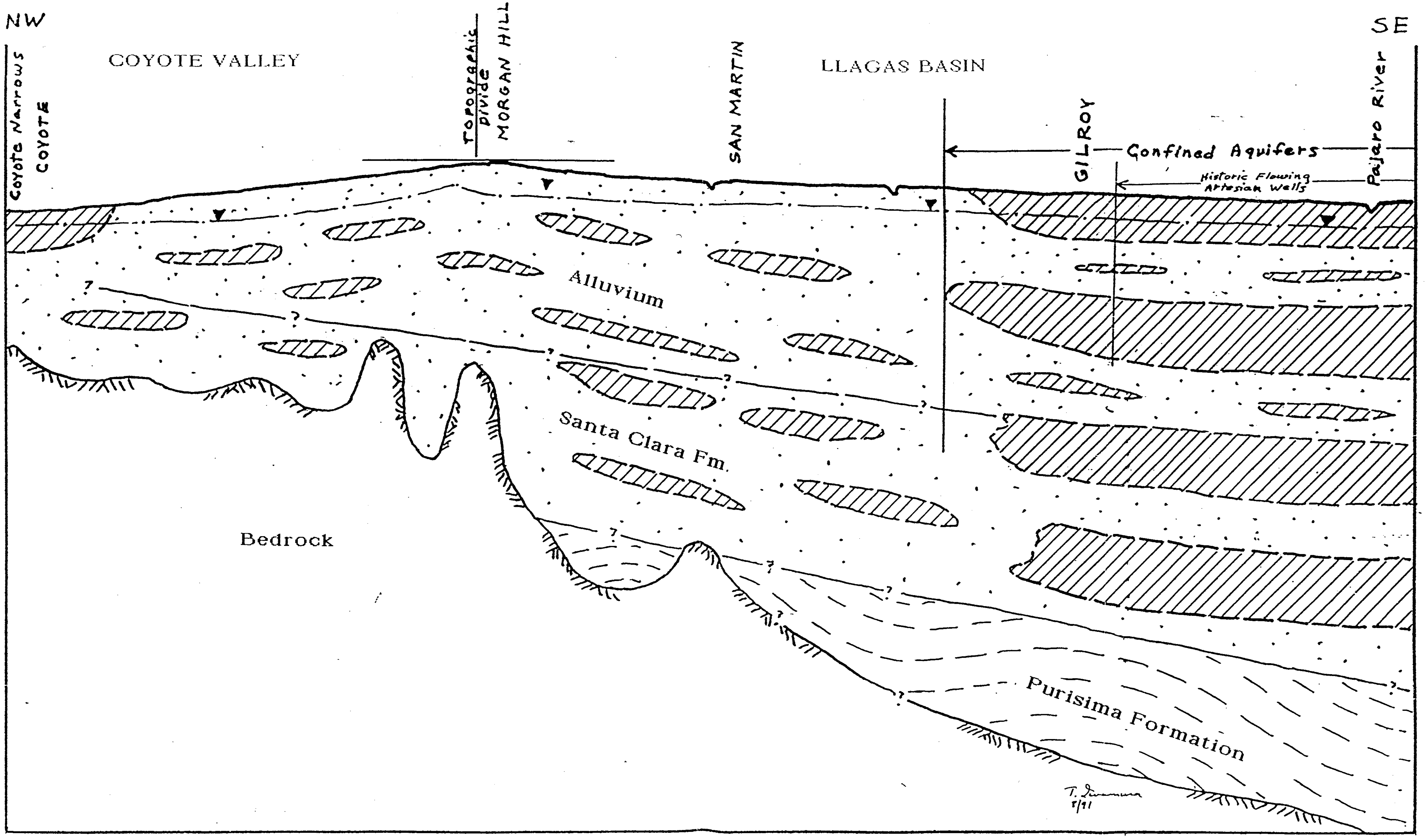
[3] Additional discussion of Llagas Basin geology and hydrogeology in available in the May 1981 ``Evaluation of Ground Water Resources: South San Francisco Bay. Volume IV: South Santa Clara County Area,'' by the Department of Water Resources (Bulletin 118-1).



Not to scale

FIGURE 2: DIAGRAMMATIC CROSS SECTION
COYOTE VALLEY - LLAGAS BASIN

IV. OBJECTIVES OF SAMPLE COLLECTION

Collecting additional groundwater samples from Llagas Basin during this phase of the study allowed us to supplement the information gathered during previous phases of the study. Current groundwater quality data enabled us to continue analysis of nitrate trends in six wells in the study area and to monitor groundwater quality in the vicinity of known nitrogen source areas. Also, two wells screened only in the shallowest groundwater zone were selected to provide depth-specific data for that zone, and two wells located outside of the valley floor of the study area were selected to provide ``background''[4] water quality data. Rainwater samples were also collected to provide information on the nitrogen content of rainwater. The following paragraphs describe these objectives in more detail and discuss the limitations associated with each.

The ``Nitrate Data Review'' report discussed historical nitrate occurrence in groundwater in the study area. That report presented areal distributions of nitrate concentrations based on historical data and illustrated nitrate trends in several wells from which many samples were collected since the late 1950s. The recent data collected allowed us to continue trend analysis in several selected wells, and to confirm the presence of nitrate in all areas of Llagas Basin. We were also able to compare the historical percentages of wells whose water contained nitrates in excess of MCLs with recent results.

A major factor considered when selecting wells for the sampling program was whether or not well construction information was available for each well. Knowing screened intervals for the majority of wells sampled as part of this study allowed us to evaluate, with limitations, the relationship between nitrate concentration and depth. By performing two rounds of sampling, we were able to investigate the changes in nitrate concentration between times of the year with all other factors held relatively constant. One of the common difficulties in reviewing historic data is attempting to account for nitrate concentration differences attributable to different field or laboratory techniques, as opposed to differences in aquifer water quality.

The ``Nitrate Source Area Identification'' report reviewed the sources of nitrate in Llagas Basin. Wells were selected for sampling both regionally upgradient and downgradient of major nitrate source areas in Llagas Basin. It was not our intent to sample in the vicinity of every nitrate source, or to infer that the areas and facilities selected are necessarily the principal contributors to the nitrate problem. Our goal was to sample in the vicinity of several known types of nitrate sources, and to see if any conclusions could be drawn regarding relative nitrate contributions from different types of sources. Given the scope of this study, we realized that we would not be able to reach definite conclusions about the contributions of specific sources due to the limitations discussed below.

Two major limitations when attempting to correlate nitrate concentrations in groundwater to nitrate sources in Llagas Basin are (1) the absence of vadose zone soil water[5] quality data, and (2) the lack of detailed hydrogeologic evaluations in the immediate vicinity of selected source areas. Further soil and groundwater investigation in the study area would be required in order to address these limitations (Rolston, et al., 1994).

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[4] These wells are considered ``background'' because their location precludes them from being affected by the dense concentration of major anthropogenic sources on the valley floor identified in the source identification phase of the study. Additionally, high recharge rates may be observed in the wells since they are located near creeks.

[5] Soil water refers to that moisture which is present in the vadose zone, above the saturated zone. Water samples from the unsaturated zone are commonly collected using a suction lysimeter, or extracting soil water from a sediment core sample (Rolston, et al, 1994a, Appendix 1, page 18).

Investigating the vadose zone helps correlate nitrate sources to nitrate occurrences in groundwater. If soil water samples collected from a borehole drilled in the vicinity of a suspected nitrate source reveal significant nitrates from the ground surface to groundwater, it follows that the nitrate in the local groundwater is likely attributable to the nearby source. Analyzing for $\delta^{15}N$ in vadose zone soil water samples can also help identify sources of nitrate in samples collected throughout the depths studied. When little or no nitrate is found during the vadose zone investigation, but significant nitrate groundwater contamination is present, migration from a distant source may be occurring. Only groundwater quality data was investigated during this phase of the study. Therefore, future work may be necessary in order to identify and confirm individual suspected sources.

Detailed hydrogeologic evaluations in the vicinity of selected wells and source areas help correlate nitrate sources to nitrate occurrences in groundwater by enabling us to track groundwater flow patterns. Although a nitrate source may be located in the immediate vicinity of a contaminated well, it may not be the source of contamination present in the aquifer. Only through investigation of groundwater flow patterns in the area of concern can one determine the areas from which well water and nitrates originate. Local hydrogeologic conditions in the vicinity of selected wells and source areas were not evaluated. Therefore, a direct correlation between nitrates in a well and a particular source could not be made.

Two shallow wells were included in our program to provide depth-specific water quality data. These wells are monitoring wells only, and are not used for water supply. However, analyzing samples from these wells allows us to draw conclusions about the vertical distribution of nitrate in the study area. Conclusions about nitrate sources can be made with fewer limitations from shallow samples, as the first-encountered water bearing zone is directly affected by the land use and facilities in the immediate area. Additionally, water in this zone has not yet mixed and traveled with water in deeper zones.

Two wells were located out of the valley floor of the study area. ``Background'' water quality samples were obtained from these wells, as they are located topographically and areally away, and hydraulically upgradient, from the concentrated anthropogenic nitrate sources identified in Llagas Basin. Although the water in these wells may not be pristine (some residential and agricultural activities occur in their vicinity), their location enables them to produce samples representative of water in south Santa Clara County outside of the main groundwater zones of the region.

Samples of rainwater were also collected from the study area to assess the nitrogen contribution from precipitation. Although estimates of this natural nitrate source were made during the source identification phase of the study, we collected field data to support our assumptions.

Methods of sample collection and analysis are described in this study's August 1992 (revised November 1993) Quality Assurance Project Plan. Procedures used to select the 28 wells in our program are described in the December 1994 ``Sample Point Selection'' report. Please refer to Figure 3 for sampling point locations.

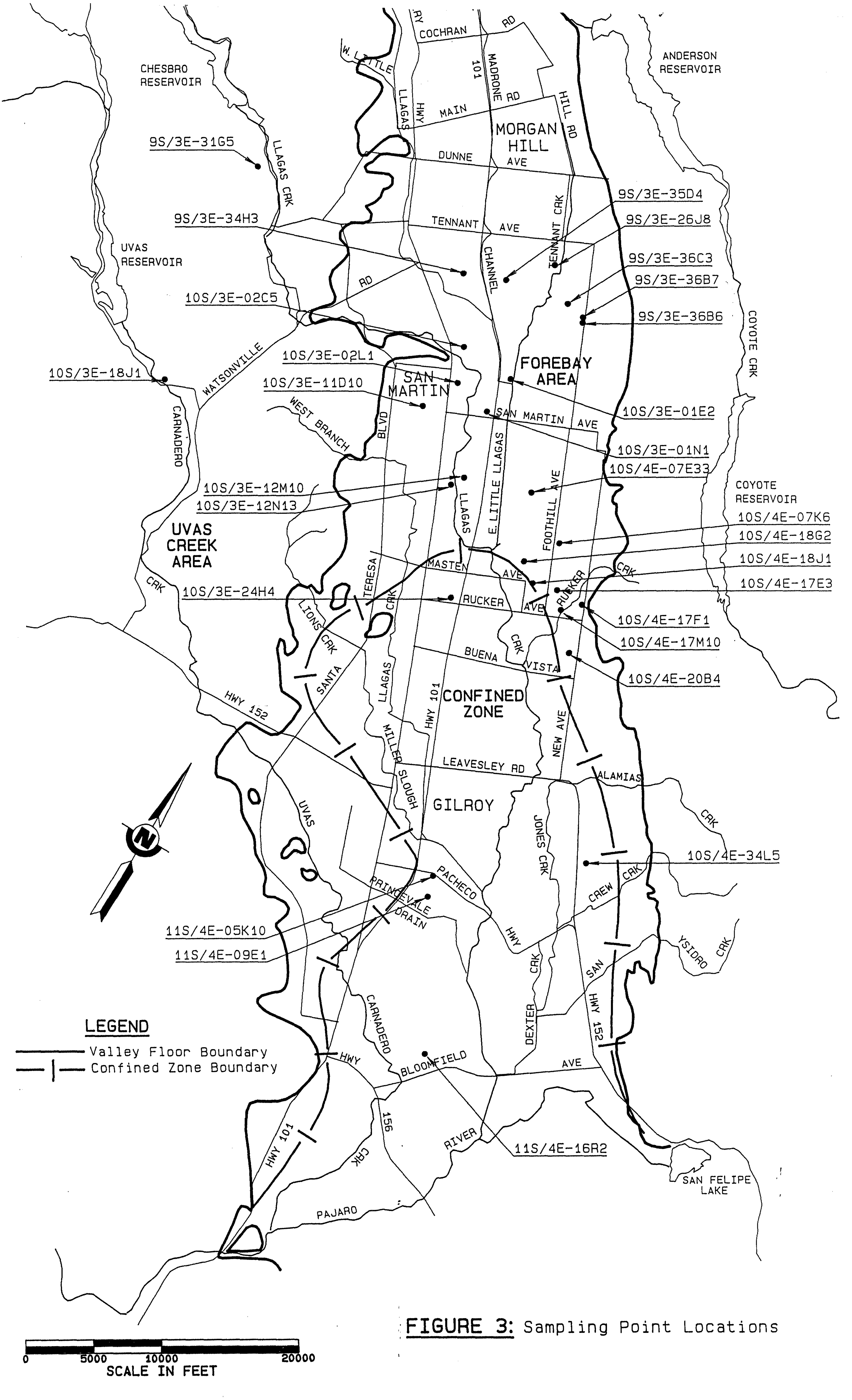

FIGURE 3: Sampling Point Locations

V. GENERAL DISCUSSION OF SAMPLING RESULTS

This section discusses general observations that can be made from reviewing just the nitrate data from our sampling events. Later sections relate the data to their location in the basin and the geology of the area, and discuss other sampling parameters.

When averaging the values obtained from our 1993 and 1994 sampling events, 7 of 28 wells, 25 percent, contained nitrates in excess of the 45 mg/l MCL. During review of historical data earlier in the study, we discovered that approximately 33 percent of the wells (278/837) with nitrate data available had produced water containing more than 45 mg/l of nitrates. The value discovered during our recent sampling (25 percent) was comparable, but somewhat lower. The two figures should not be given equal importance though, as the sample size for our historical evaluation was much greater. The data collected during this phase of the study was gathered to supplement historic data; the combination provides a statistically sound sample size to help in our development of a nitrate management plan.

Also, Figure 4 and Tables 1 and 2 illustrate that the concentrations detected during our February/March 1994 sampling were generally higher than those detected in December 1993. Only five wells exhibited nitrate concentrations which decreased or remained the same from one sampling event to the next; the remainder increased. The average percent difference between nitrate concentrations from the first to the second sampling event was +15 percent. The average absolute value of percent differences between the two rounds was 18 percent[6]. The relatively low average absolute value of percent differences between the two sampling rounds illustrates the generally good agreement between sampling rounds. The fact that the average percent difference and the average absolute value of percent differences are nearly identical points out the consistency of increased nitrate concentrations apparent in all the wells from the first sampling round to the second. Our sampling was not without wide fluctuations, however. Two wells showed an approximate 100 percent increase from the first sampling round to the next. This was the exception rather than the rule. The general increase from December to February/March may be due to downward migration of nitrate contained in vadose zone soil water induced by winter percolation. It may also be due to the migration of groundwater containing different nitrate concentrations through the zones in which the wells are completed. Variations in sample handling or laboratory error may have also contributed to differences from one sample round to the next.

As seen in Tables 1 and 2, two sets of nitrate data exist for each sampling round. One set of results was obtained from a local laboratory; the other was obtained from an out-of-state laboratory.

It is important to note that the above evaluations were based on the nitrate concentrations obtained from the local laboratories used for the study. Nitrate concentration data from the University of Illinois at Urbana-Champaign (UIUC) were produced as part of the $\delta^{15}N$ analysis, and did not result from nitrate analysis alone. Some of the concentrations reported by UIUC were orders of magnitude different from expected values or those suggested by other samples from the same well, and the results are suspect. Further inspection of the results and chain of custody forms revealed that all results from UIUC for samples collected on March 2 and March 7, 1994 were affected. Nitrate concentrations from March 1994

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[6] Percent differences between the December 1993 and the February and March 1994 nitrate concentrations for each well were calculated by dividing the difference between the sampling round results (February and March 1994 minus December 1993) by the December 1993 result. To calculate the average percent difference, these values were added (including whether the values were positive or negative) and divided by the total number of wells. To calculate the average absolute value of percent differences, the absolute value (discounting whether the values were positive or negative) was averaged similarly. If these two calculations yielded the same result, that would indicate an increase in nitrate concentrations was observed in all wells sampled.

(Curtis & Tompkins) for well No. 11S/04E-05K10 were 140 mg/l, for example. The March 1994 result from Illinois was 1.7 mg/l. December 1993 results from UIUC and Curtis & Tompkins were 97 and 140 mg/l, respectively.

Results from Illinois for $\delta^{15}N$ for the days in question were also well outside the range of typical $\delta^{15}N$ values reported in literature. The suspect results ranged as low as -13.09; only one of more than 40 studies cited in the referenced Rolston, et.al., reports discovered $\delta^{15}N$ values lower than -10.00.

Neither UIUC nor our sampling contractor could explain the apparently erroneous data. The nitrate and $\delta^{15}N$ results from UIUC for samples collected on March 2 and 7, 1994, were not used for evaluation in this report. There appear to be no errors associated with any of the analyses besides the March 2 and 7 samples which were sent to UIUC. Therefore, nearly all of the data collected during our two sampling rounds was used during data evaluation. Any evaluations incorporating $\delta^{15}N$ results in this report only incorporate results from the December sampling event. Although not all of the March results are suspect, we did not want to compare a single result from a well with an average of two results from another well.

Samples of rainwater were also collected and analyzed during the sample collection phase of the study to supplement the groundwater samples collected. Sample bottles positioned at the Santa Clara Valley Water District's South County Meter Shop, located near the geographic center of the study area, were allowed to fill with rainwater during a storm event. These samples were found to not contain detectable concentrations of ammonia, TKN, or nitrite. Nitrate was detected at 0.9 mg/l (expressed as nitrogen). This concentration is in general agreement with the value used as a rainwater estimate in our ``Nitrate Source Area Identification'' report, 1.3 mg/l. The nitrate concentration detected during our recent sampling further supports our previous conclusion that rainwater is a minor contributor of nitrogen to Llagas Basin, since that concentration is lower than the one used for our previous source calculation.

TABLE 1: Sample Results - Sampling Round 1 (December 1993)

Well I.D.	Well Purpose	Well Type	Reported Depth (feet)	Reported Screen(s) (feet bgs)	Nitrate # (Illinois)	Nitrate (Sequoia)	Nitrate + Nitrite # (C & T)	Nitrite	Dissolved Ox.	Delta 15-N	Delta 18-O	TKN	Ammonia	Chloride	Total Coliform (colonies / 100 mL)
10S3E01E2	E	domestic	250		68		81		7.17	3.53	-5.80			42	
10S4E18J1	E	domestic	180		33		36		11.73	3.41	-6.00			45	
10S4E34L5	E	ag. and domestic	163		65	75		nd	8.01	2.51	-6.05			70	
9S3E35D4	T	domestic			30		33		8.81	0.10	-6.04			32	
10S4E17F1	T	domestic	360	240-360	2.0		3.0		0.24	7.36	-6.31			36	
10S4E18G2	T	agricultural	130		32		37			2.02	-6.22			32	
10S3E02C5	F	domestic	200	140-200	17		21			-1.09	-7.45			80	
10S3E02L1	F	domestic	187		25		31		5.82	4.73	-5.31			28	
9S3E36B7	SDP	domestic	225	165-225	26	33		nd	7.80	1.27	-5.97			90	
9S3E36C3	SDP	domestic	220	100-120; 140-160; 180-220	45		81		10.08	-1.14	-5.90			130	
11S4E09E1	STP	domestic	400	130-210; 250-310; 350-390	56	68		nd	10.15	2.10	-5.79	nd	nd	30	
11S4E16R2	STP	agricultural	480	270-320; 340-360; 450-470	17		34		16.66	8.40	-5.78	nd	nd	70	
10S3E11D10	W	ag. and domestic	181	80-100; 121-141; 161-181	33		41		6.98	0.39	-5.60			28	
10S3E12N13	W	muni. and indust.	126	116-126	4.3	6.8		nd	4.22	4.23	-5.06			33	
10S3E12M10	W	muni. and indust.	200	120-200	20		23		9.00	3.98	-5.37			15	
10S4E17M10	D	domestic	210	80-210	29		31		11.18	3.04	-6.25			46	
10S4E20B4	D	domestic	220	55-220	13		15		4.41	2.21	-5.82			40	
9S3E34H3	SM	ag. and domestic	200	112-135; 178-184	24		28		7.59	1.44	-7.78		nd	44	
9S3E26J8	SM	domestic	175	135-175	55		63		8.47	2.59	-6.47		nd	60	
10S3E24H4	SM	domestic	200	85-180	17		19		5.05	3.57	-5.86		nd	16	
10S4E17E3	SM	domestic	200	180-200	37		41		10.08	3.24	-5.91		nd	43	
9S3E36B06	SM	domestic		185-225	27	32		nd	6.91	2.85	-6.21		nd	70	
10S3E01N1	S	monitoring	30	10-30	62		72		7.37	0.14	-5.75		nd	34	na - interference
11S4E05K10	S	monitoring	35.5	10-35	97		140		6.71	-0.38	-5.44		nd	33	na - interference
10S4E07K6	AF	domestic	237	187-237	22		24		8.41	1.95	-6.23			46	na - interference
10S4E07E33	AF	domestic	228	180-228	38		24		3.72	2.52	-5.88			34	<1
10S3E18J1	BK	domestic			0.05	1.2		nd	8.43	insuff. N	-5.36	0.9	nd	40	
9S3E31G5	BK	domestic	55	20-30; 45-55	0.9	2.5		nd	0.71	insuff. N	-4.82	na	nd	21	
				Detection Limits:	N/A	0.1	0.04*	0.1	N/A	N/A	N/A	0.5	1*	0.5	N/A

E = Example Wells
T = Trend Wells
F = Food Processor
SDP = Sewage Disposal Pits
STP = Gilroy Sewage Treatment Plant
W = Winery

D = Dairy
SM = San Martin Special Use Area
S = Shallow Monitoring Wells
AF = Agricultural Field
BK = Background area

All results reported in mg/L as the analyte (Nitrate as Nitrate, etc.)
nd = not detected
na = not analyzed
blank spaces = not collected
see text and appendices for units of 15N and 18O analyses

= results originally reported as Nitrogen (x 4.5 = as Nitrate)
* = detection limit when reported as Nitrogen
N/A = Not applicable
Dissolved Ox. originally reported as O2 % (O2% x .0914 = mg/L)

TABLE 2: Sample Results - Sampling Round 2 (February/March 1994)

			Reported Depth	Reported Screen(s)	Nitrate #	Nitrate #	Nitrite ^	Dissolved Ox.	Delta 15-N	Delta 18-O	TKN	Ammonia	Chloride	Total Coliform	Fecal Coliform	E-Coli
Well I.D.	Well Purpose	Well Type	(feet)	(feet bgs)	(Illinois)	(C & T)								(MPN / 100 mL)	(MPN / 100 mL)	(MPN / 100 mL)
10S3E01E2	E	domestic	250		3.3	86	nd	14.1	-13.09	-5.84			39			
10S4E18J1	E	domestic	180		32	32	nd	8.6	2.98	-5.02			40			
10S4E34L5	E	ag. and domestic	163		0.77	81	nd	9.8	-11.67	-5.74			60			
9S3E35D4	T	domestic			33	39; 38	nd; nd	6.4	-1.89	-5.82			32; 34			
10S4E17F1	T	domestic	360	240-360	0.86	2.7	nd	8.6	3.44	-6.24			40			
10S4E18G2	T	agricultural	130		29	30	nd	2.8	3.22	-6.26			30			
10S3E02C5	F	domestic	200	140-200	19	23	nd	7.4	.14	-7.12			60			
10S3E02L1	F	domestic	187		28	33	nd	5.8	3.50	-5.50			25			
9S3E36B7	SDP	domestic	225	165-225	1.1	33; 33	nd; nd	8.2	-5.88	-5.87			60			
9S3E36C3	SDP	domestic	220	100-120; 140-160; 180-220	1.6	99	nd	9.23	-5.79	-5.58			110			
11S4E09E1	STP	domestic	400	130-210; 250-310; 350-390	4.2	72	nd	9.8	-11.60	-5.49	nd	nd	25			
11S4E16R2	STP	agricultural	480	270-320; 340-360; 450-470	0.0	26	0.69	3.6	insuff. N	-5.52	nd	nd	60			
10S3E11D10	W	ag. and domestic	181	80-100; 121-141; 161-181	3.0	43	nd		-10.26	-5.44			27			
10S3E12N13	W	muni. and indust.	126	116-126	6.1	8.1	nd	4.62	3.18	-5.14			22			
10S3E12M10	W	muni. and indust.	200	120-200	4.3	25	nd	6.6	-5.58	-6.27			14			
10S4E17M10	D	domestic	210	80-210	2.3	33	nd	8.4	-9.36	-6.27			32			
10S4E20B4	D	domestic	220	55-220	16	18	nd	2.9	2.24	-6.14			40			
9S3E34H3	SM	ag. and domestic	200	112-135; 178-184	24	29	nd	6.6	-.09	-6.42		nd	41			
9S3E26J8	SM	domestic	175	135-175	3.2	68	nd	10.8	-8.20	-6.21		nd	60			
10S3E24H4	SM	domestic	200	85-180	17	21	nd	5.4	2.91	-5.22		nd	15			
10S4E17E3	SM	domestic	200	180-200	36	42	nd	10.3	1.43	-5.87		nd	44			
9S3E36B06	SM	domestic		185-225	1.0	33	nd	8.0	-8.79	-6.09		nd	50			
10S3E01N1	S	monitoring	30	10-30	4.5	99	nd	8.0	-12.44	-6.17		nd	38			
11S4E05K10	S	monitoring	35.5	10-35	1.7	140	nd	7.0	-11.30	-5.16		nd	29	16.1	5.1	2.2
10S4E07K6	AF	domestic	237	187-237	2.1	27	nd	9.6	-10.36	-6.49		nd	39	1.1	1.1	1.1
10S4E07E33	AF	domestic	228	180-228	3.1	50	nd	9.2	-10.82	-5.91			27	2	<1.1	<1.1
10S3E18J1	BK	domestic			.23	1.7	nd	13.16	0.13	-5.02			9	<1.1	<1.1	<1.1
9S3E31G5	BK	domestic	55	20-30; 45-55	0.0	5.0	nd	7.8	insuff. N	-4.68	nd	nd; nd	20; 20			
				Detection Limits for well samples:	N/A	0.04*	0.02*	N/A	N/A	N/A	1	1*	0.5 or 1	N/A	N/A	N/A
	Rainwater					4.0	nd				nd	nd				
				Detection Limits for rain sample:		2.2	1.6				1	1*				

E = Example Wells
T = Trend Wells
F = Food Processor
SDP = Sewage Disposal Pits
STP = Gilroy Sewage Treatment Plant
W = Winery

D = Dairy
SM = San Martin Special Use Area
S = Shallow Monitoring Wells
A = Agricultural Field
BK = Background area

All results reported in mg/L as the analyte (Nitrate as Nitrate, etc.)
nd = not detected
na = not analyzed
blank spaces = not collected
see text and appendices for units of 15N and 18O analyses

= results originally reported as Nitrogen (x 4.5 = as Nitrate)
^ = results originally reported as Nitrogen (x 3.3 = as Nitrite)
* = detection limit when reported as Nitrogen
N/A = Not applicable
2 results in same box indicate duplicate sample analysis

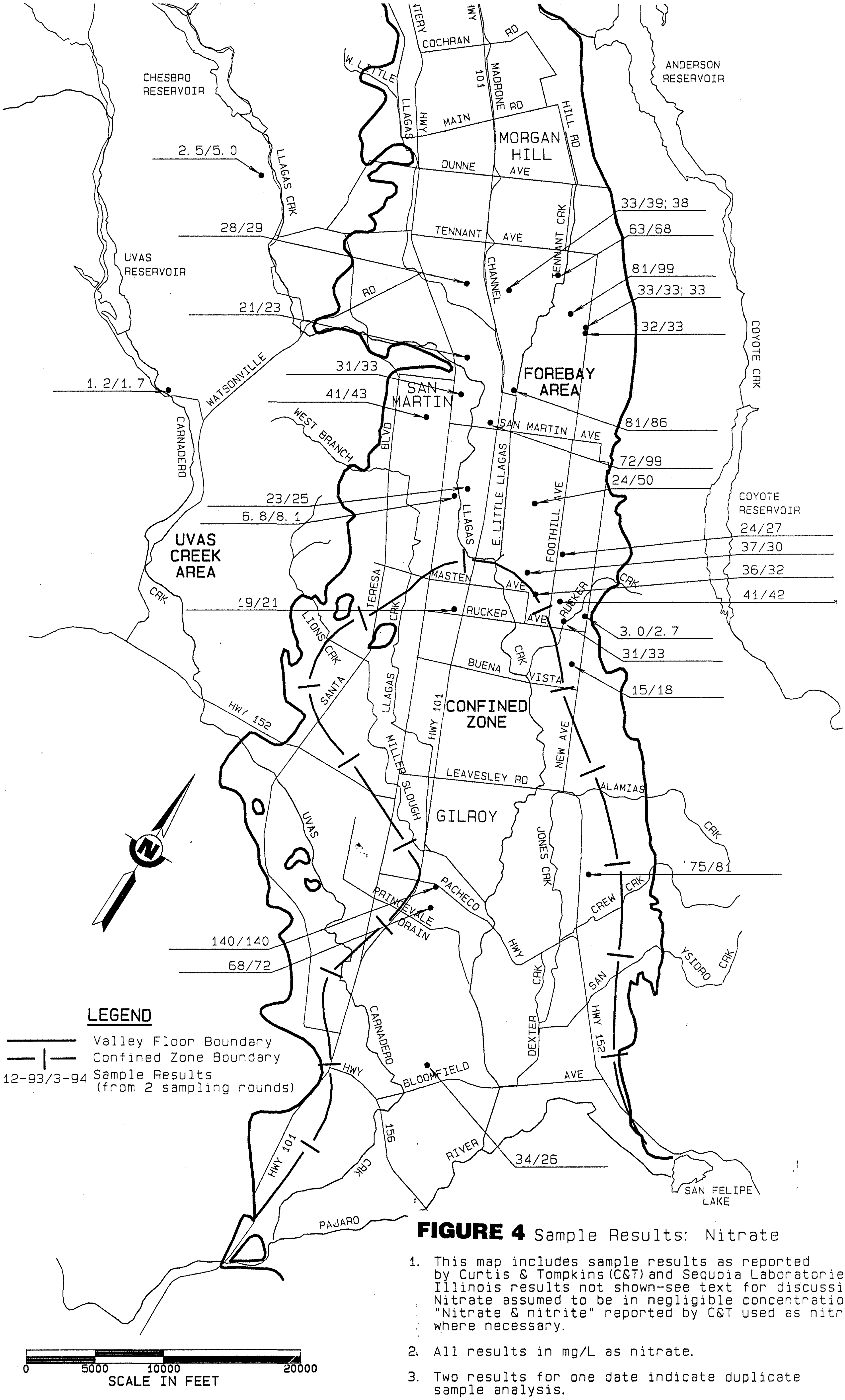


FIGURE 4 Sample Results: Nitrate

1. This map includes sample results as reported by Curtis & Tompkins (C&T) and Sequoia Laboratories. Illinois results not shown-see text for discussion. Nitrate assumed to be in negligible concentrations; "Nitrate & nitrite" reported by C&T used as nitrate where necessary.

2. All results in mg/L as nitrate.

3. Two results for one date indicate duplicate sample analysis.

VI. AREAL DISTRIBUTION OF NITRATES

Several conclusions regarding the areal distribution of nitrates can be drawn from the data collected during our two sampling rounds in December 1993 and February and March 1994. The focus of these conclusions is on locations and percentages of wells producing water with nitrate exceeding drinking water MCLs, and on the location of nitrate contamination relative to hydrogeologic boundaries.

First, wells producing nitrate-laden water in excess of the federally mandated MCL are currently found in all areas of Llagas Basin. This observation is consistent with historical data, and also confirms the persistence of nitrates in the study area. Figure 4 illustrates the nitrate concentrations found in groundwater from each well during December 1993 and February and March 1994. As seen in Figure 4, the most northerly wells in the program, located roughly between Morgan Hill and San Martin, produced water containing up to 99 mg/l of nitrate. The wells located in the confined zone, towards the southern portion of the study area, produced water containing up to 140 mg/l. Although not containing nitrate exceeding the MCL, the most southerly well in our study area produced water containing up to 34 mg/l, just 11 mg/l below the federal MCL. Also, nitrates above MCLs were not detected in any of our wells located in the western side of the valley, west of Highway 101. However, these wells were not free of nitrates, as six of these seven wells did contain more than 20 mg/l, up to 43 mg/l.

Second, the historical distribution of nitrates in the study area relative to the confined/unconfined boundary showed that while nitrates in excess of MCLs were located throughout the basin, the highest concentrations (70 mg/l and greater) were found primarily in wells located in the confined zone. This trend was confirmed by our recent sampling events. Of the wells in the confined zone, 60 percent (3/5) contained nitrate concentrations above 45 mg/l, while only 17 percent (4/23) of the wells located north of the confined/unconfined boundary contained such water. Discounting results from our ``background'' wells, 60 percent (3/5) of the wells in the confined zone produced nitrates exceeding 70 mg/l, while only 14 percent (3/21) of the wells located in the unconfined zone produced nitrates exceeding 70 mg/l. It is important to note that due to our priority of selecting wells near source areas, and due to the relatively low number of wells in the southern portion of Llagas Basin, significantly fewer samples were collected from the confined zone than from the unconfined zone. Additional sampling from the confined zone would provide additional data to strengthen conclusions concerning the areal distribution of nitrates in the study area.

Third, all samples collected from the shallow monitoring wells were found to contain nitrates exceeding 70 mg/l, up to 140 mg/l. One of these wells is located in the confined zone; the other is located north of the confined/unconfined boundary. Further discussion of results from these wells is discussed in the ``Vertical Distribution of Nitrates'' section.

VII. VERTICAL DISTRIBUTION OF NITRATES

Previous studies have found correlations between nitrate concentrations and depths of wells in regional groundwater systems (Eccles and Bradford, 1977; Eccles and Klein, 1978). Although the scope of our study did not allow for (1) the installation of monitoring wells designed to collect samples from specific depths in the basin and (2) detailed hydrogeologic investigations, we investigated this relationship to the extent feasible. Also, we made an effort to select wells for sampling whose construction details were available. Several of these wells have multiple perforations; therefore, samples from them are most likely a mix of water from two or more aquifers and cannot provide us with depth-specific water quality data. Wide screening intervals can also have the same effect. Sanitary seal information for many of the wells was not available, and older seals may be compromised. The intrusion of shallow groundwater into water wells can also reduce the likelihood that aquifer-specific samples are being obtained.

Two wells screened only in the shallowest water bearing zone were selected for our sampling program in order to determine nitrate and other constituent concentrations in that zone at two points. We believe that samples collected from these wells are representative of water at their screening depths. Shallow wells are less likely than deep wells to be affected by water from zones other than their reported screened interval; proportionally, they have much less of their length available for infiltration, cascading, or other hydraulic breaches of well integrity. Both of the shallow wells in our sampling phase produced significantly contaminated water. The four samples collected from these wells and analyzed by local laboratories contained 72, 99, 140, and 140 mg/l of nitrate. Nitrates in similar concentrations have been detected in shallow monitoring wells at the Gilroy-Morgan Hill Municipal Wastewater Facility (RWQCB, 1994).

Wells reportedly screened in only a deeper water bearing zone, on the other hand, generally showed lower, but not insignificant, nitrate concentrations. Among twelve samples from six wells screened only below 180 feet below ground surface, for example, none contained nitrates in excess of MCLs. Four of these six wells are located just north of the confined/unconfined boundary; one is located further north in the unconfined zone. One of the wells, 11S/04E-16R02, is located in the confined zone. This well is reportedly screened only below 270 feet below ground surface. The average nitrate concentration in water from this well during our sampling program was 30 mg/l. The results from the six deep wells indicate that significant nitrate contamination, although below MCLs, can be found in deeper groundwater, even underneath the confining layer, of the study area. The average concentration of these samples was 28 mg/l, while the average concentration from the shallow wells was 113 mg/l. Figures were developed which illustrate (1) the top and (2) the midpoint of the reported screened interval for each well in our study versus the average nitrate concentration detected during the two sampling rounds. Nitrate concentrations were also plotted against total well depth. A loose correlation indicating that nitrate concentrations decrease with depth of perforated interval was evident. Please refer to Figures 5 through 7.

The above evaluations indicate that significant nitrate concentrations may be less likely found at significant depths in Llagas Basin. However, the fact that nitrates were present in deep wells in concentrations up to 50 mg/l shows that nitrate contamination is by no means solely a shallow groundwater problem. Nitrate travels readily with groundwater and has likely been percolating in the study area for decades. The study area also is known to contain numerous older, abandoned, and lost wells which have likely aided in the vertical migration of nitrates to all depths of Llagas Basin (Rolston et al., 1994b, pp. 11-12).

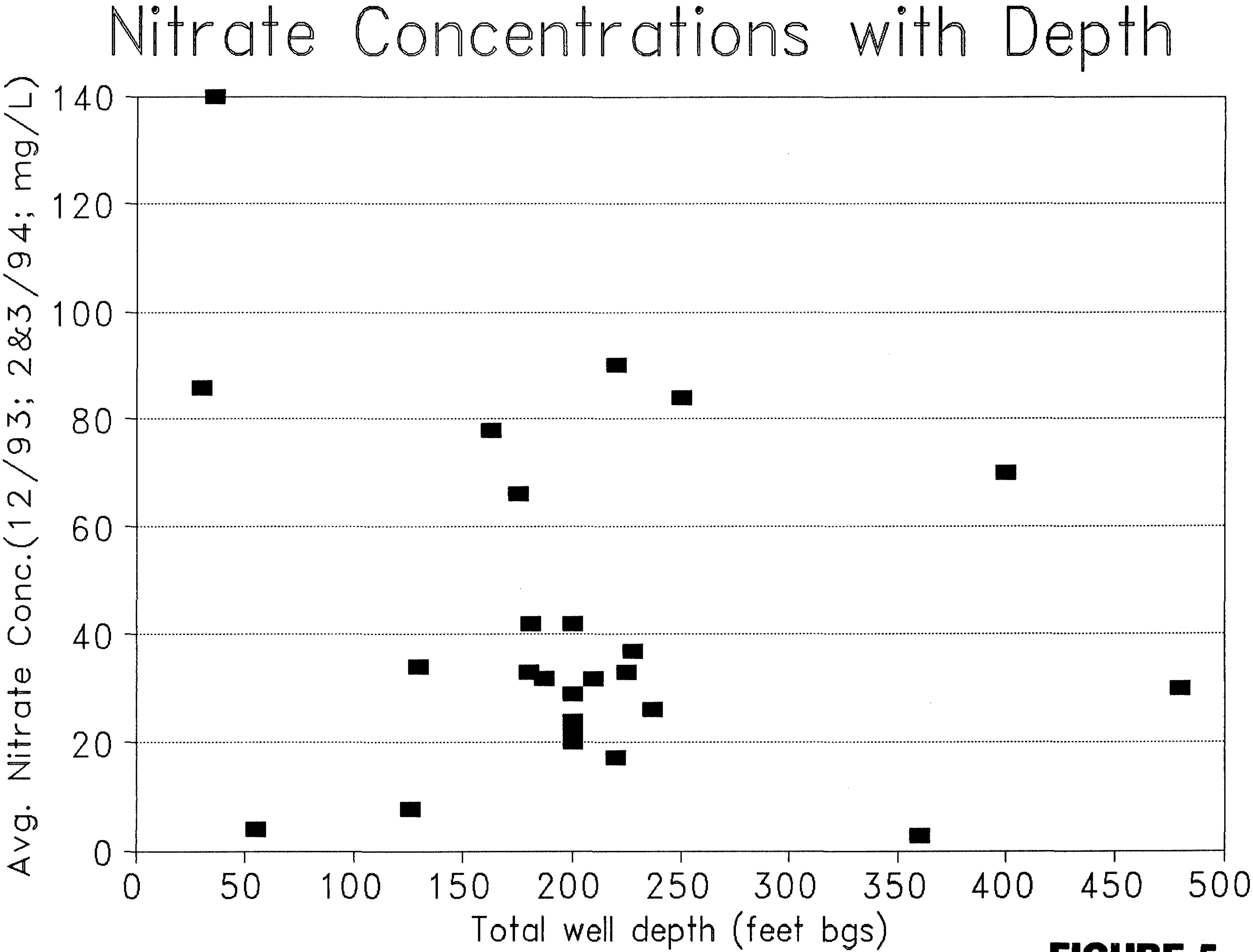

Nitrate Concentrations with Depth
Avg. Nitrate Conc.(12/93; 2&3/94; mg/L)
0
20
40
60
80
100
120
140
0
50
100
150
200
250
300
350
400
450
500
Total well depth (feet bgs)

FIGURE 5

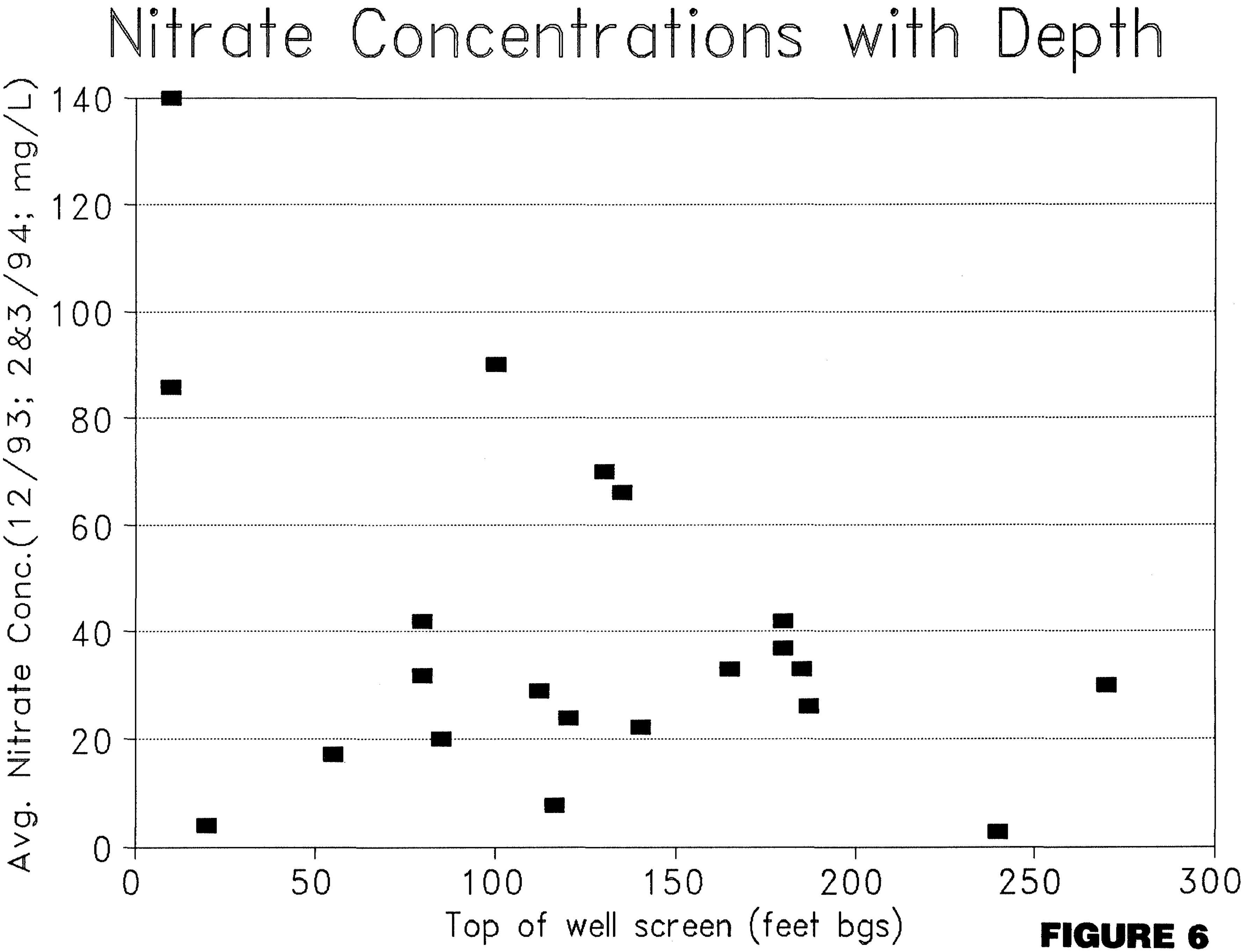
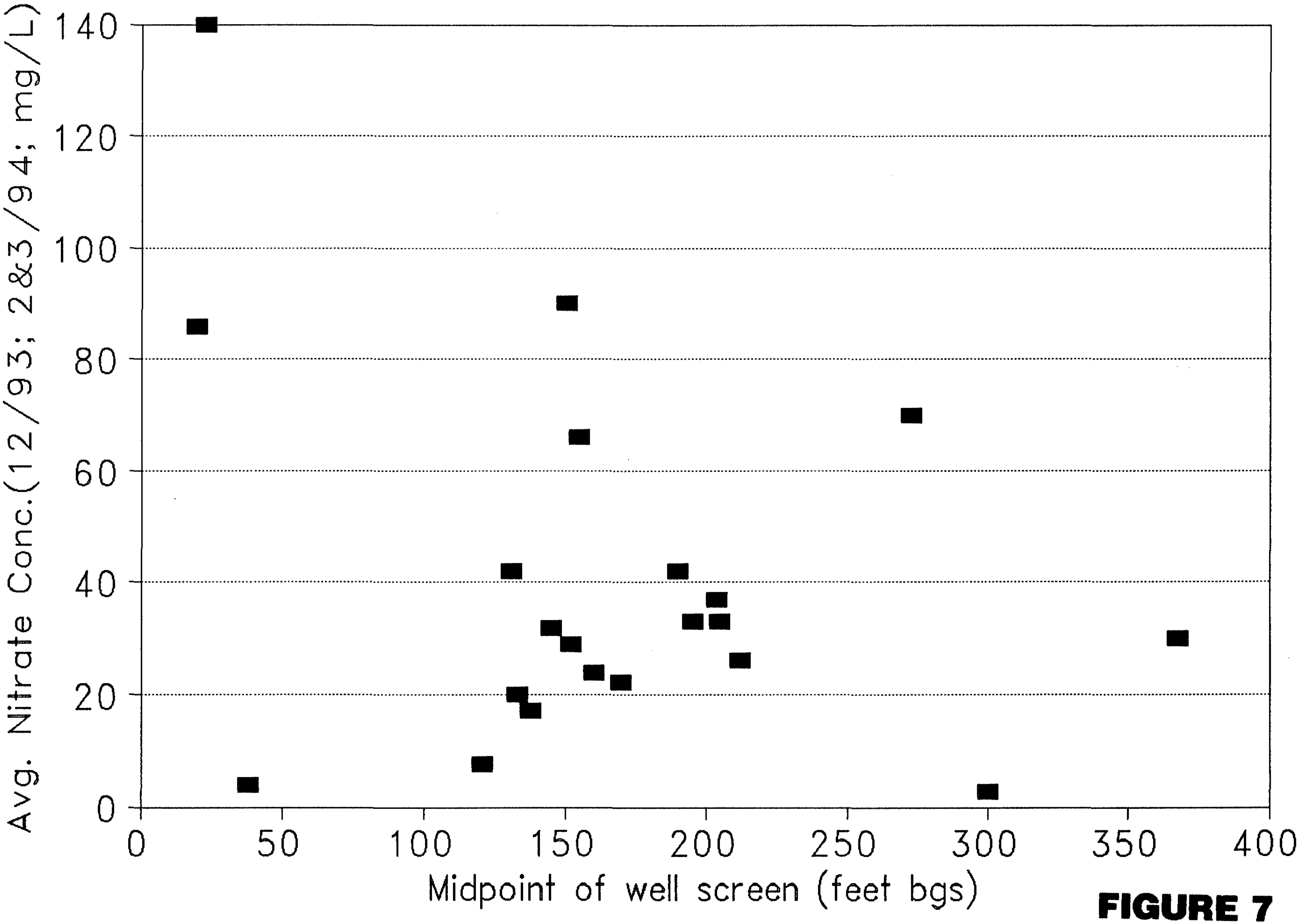

Nitrate Concentrations with Depth
Avg. Nitrate Conc.(12/93; 2&3/94; mg/L)
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
Top of well screen (feet bgs)

FIGURE 6



Nitrate Concentrations with Depth

FIGURE 7

VIII. TREND ANALYSIS

One major purpose of our sampling program was to continue trend analysis for those wells with significant historical nitrate data. In this study's ``Nitrate Data Review'' report dated August 1993, a general increasing trend of nitrate concentrations was evident in the six wells used for trend analysis. Samples from the late 1950s through the early 1990s were incorporated into this evaluation. Only three of these wells were available for resampling during our investigation; these are known as ``example wells'' in previous reports. Three wells whose trends were not graphed in our previous report were selected for sampling in 1993 and 1994; these are known as ``trend'' wells in previous reports. Figures 9, 10, and 12 show trends from the ``example'' wells. Trends from the three ``trend'' wells are shown in Figures 8, 11, and 13.

Results from the six wells recently sampled for trend analysis purposes confirmed the fact that nitrate is still present in these wells. Also, all of the results fell within the ranges of historical concentration data. Please refer to Table 3.

When evaluating the data in more detail, samples from two of these wells indicated that, although nitrate concentrations fell within the ranges of historical data they were lower than would be expected from the extrapolation of historical results. Well Nos. 10S/04E-17F01 (Figure 8, ``trend'' well) and 10S/04E-18J01 (Figure 9, ``example'' well) fall into this category. These two wells are located in close proximity to each other, just north of the confined/unconfined zone boundary. In Figure 8, a generally increasing trend was apparent from the samples collected from 1958 through 1978. Nitrate concentrations in the recent samples, however, were significantly less than concentrations reported from the 1970s to the 1980s, and are more reflective of nitrate concentrations observed from the 1950s to the 1960s. A similar situation is apparent in samples collected from 10S/04E-18J01; concentrations appear to mirror those seen twenty years ago. It is possible that the discontinuation of a significant nitrate source in this area occurred in the past, and nitrate concentrations in these wells are reflecting that event. This phenomenon may also be due to the flow of a slug of nitrate through the well location.

Recent nitrate concentrations in one of the ``example'' wells (10S/3E-01E02, Figure 10) were the highest historical nitrate concentrations reported for that well. While previous data indicated concentrations in the water from the well had only slightly exceeded 45 mg/l on two occasions, the recent sampling results were as high as 86 mg/l. This well is located in the San Martin area, and its results may reflect a land use change in a similar fashion to the wells whose results are illustrated in Figures 8 and 9.

Results from the three ``example'' and ``trend'' wells whose results are illustrated in Figures 11 through 13 generally support the gradually increasing extrapolated trend line suggested by historical sampling results. These three wells are distributed from north to south in the basin; they are located just north of the unconfined/confined border, in the confined zone, and in the unconfined zone, respectively. This may indicate that land uses in these areas are relatively constant, and may have contributed steady amounts of nitrogen to the subsurface. The theory that nitrate contamination is present in localized pockets is somewhat supported by the areal proximity of three of our ``example'' and ``trend'' wells to each other. Wells 10S/04E-18J01, 10S/04E-18G02, and 10S/04E-17F01 are all located on the east side of Highway 101, just north of the confined/unconfined boundary. Recent results from 10S/04E-17F01 and 10S/04E-18J01 were lower than would be expected from the extrapolation of historical results. Recent results from 10S/4E-18G02, however, support the gradually increasing trend line extrapolated from historical sampling results.

Conclusions cannot be drawn about the trend of nitrate **throughout** the entire basin, as only a relatively low number of wells have been included in the trend analysis during this study. Our recent sampling results indicate that trends are not identical in our ``example'' and ``trend'' wells. However, a generally increasing trend is still suggested by best fit lines for each well evaluated, using all data available. Expected scatter in the data has not altered the suggested trends.

The persistence of nitrate is evident in the wells included in our recent sampling. Unfortunately, the wells for which we have a great number of sampling results are generally lacking in well construction information. Depth-specific nitrate trends can therefore not be developed from these wells. However, general observations can be made based on the limited information available, such as total well depth.

Many variables in historical data preclude us from drawing more definitive conclusions regarding nitrate trends in the study area. These include variability in source contributions as alluded to above, variability in sampling and analysis over time, and lack of certainty regarding the depth(s) from which each ``example'' or ``trend'' well is drawing water.

TABLE 3
NITRATE CONCENTRATIONS FOR EXAMPLE AND TREND WELLS USED IN TREND ANALYSIS

Year	Well ID No. 10S4E17F1	Well ID No. 10S4E18J1[8]	Well ID No. 10S3E01E2[8]	Well ID No. 10S4E18G2	Well ID No. 10S4E34L5[8]	Well ID No. 9S3E35D4
1957			6.7			
1958	3.1	13	19		32	
1959	3.5	15	19		32	
1960	2.9	13	22		33	
1961		17	42			
1962	1.4	10	24	18	43	
1963	3.6		13	17	35	
1964	8.5	8.5	11	22	32	
1965			50			
1966			26	28	34	
1967			33			
1968		16	34	26	56	
1969						
1970						
1971	11	17	34	28	52	
1972					62	
1973	12	28		35	43	32
1974					73	31[1]
1975	15[2]	34[2]	38[3]	34[2]	48	23[7]
1976	10	42	44	38	57	
1977	10	45	38	21	62	
1978	11	40	27	37	92	44
1979					64[4]	
1980			32[5]			24
1981						
1982						
1983						
1984						
1985			46		78[5]	
1986						

TABLE 3
NITRATE CONCENTRATIONS FOR EXAMPLE AND TREND WELLS USED IN TREND ANALYSIS (continued)

Year	Well ID No. 10S4E17F1	Well ID No. 10S4E18J1[8]	Well ID No. 10S3E01E2[8]	Well ID No. 10S4E18G2	Well ID No. 10S4E34L5[8]	Well ID No. 9S3E35D4
1987						
1988	15		38[5]			
1989						
1990						
1991			27[5]		81[5]	
1992						
1993[6]	3.0	36	81	37	75	33
1994[6]	2.7	31.5	85.5	29.7	81	38.7

Notes:

[1] Average of 10 samples of similar concentration collected during 1974.

[2] Average of two samples of similar concentration collected during 1975.

[3] Also 46.5 mg/l sample collected later in the year.

[4] Actually collected in 1978 (after 92 mg/l sample).

[5] Sample result added to table since August 1993 "Nitrate Data Review" report, upon recent availability of data.

[6] 1993 and 1994 District sampling results as reported by Curtis and Tompkins (C&T) and Sequoia Laboratories (Illinois results not included in this table—see text for discussion). Nitrite assumed to be in negligible concentrations. Nitrate & Nitrite reported by C&T used as Nitrate here.

[7] Two 23 mg/L samples collected in 1975—August and October.

[8] "Example Well"—also used in "Nitrate Data Review" report.

Nitrate Trends in Well #10S4E17F1

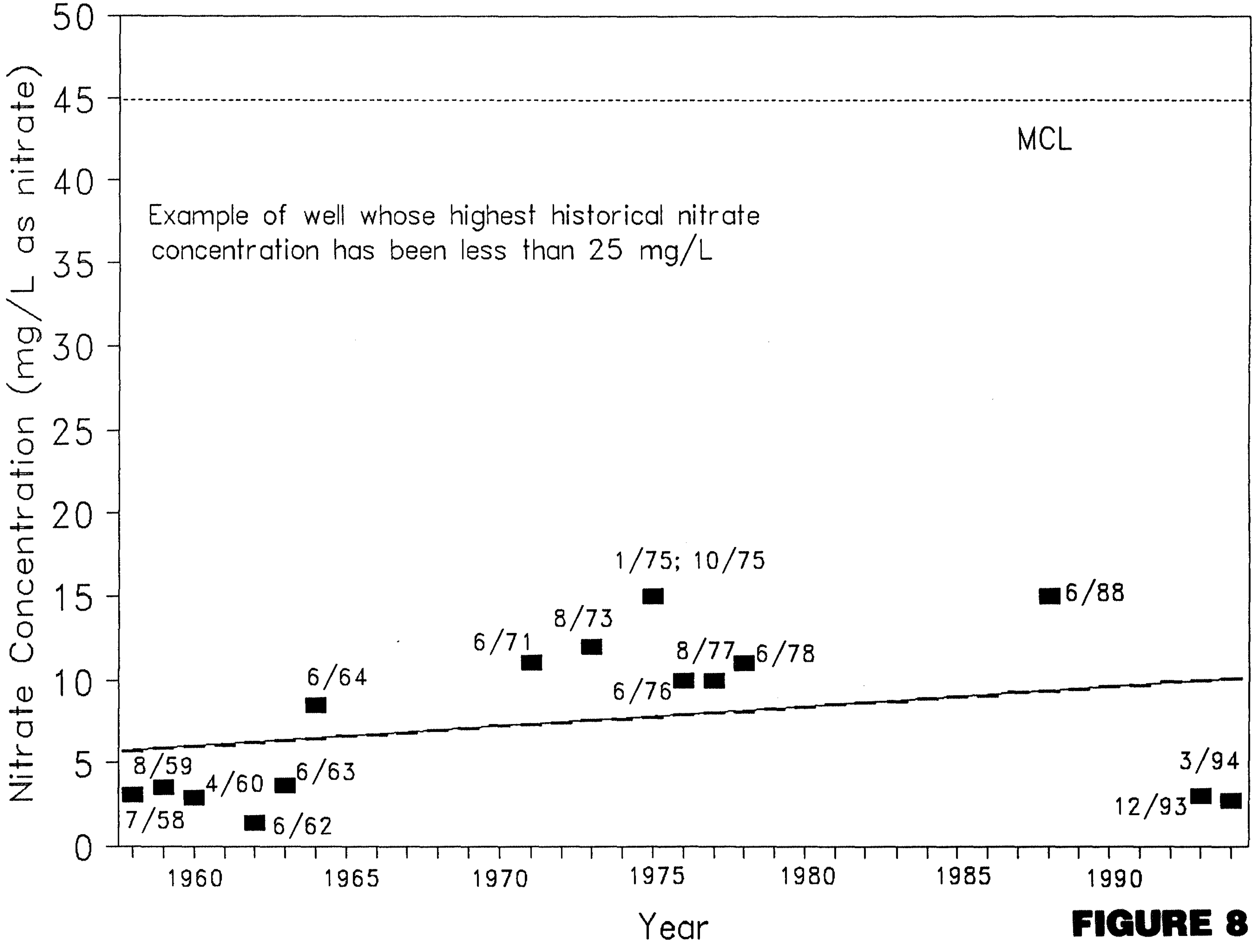
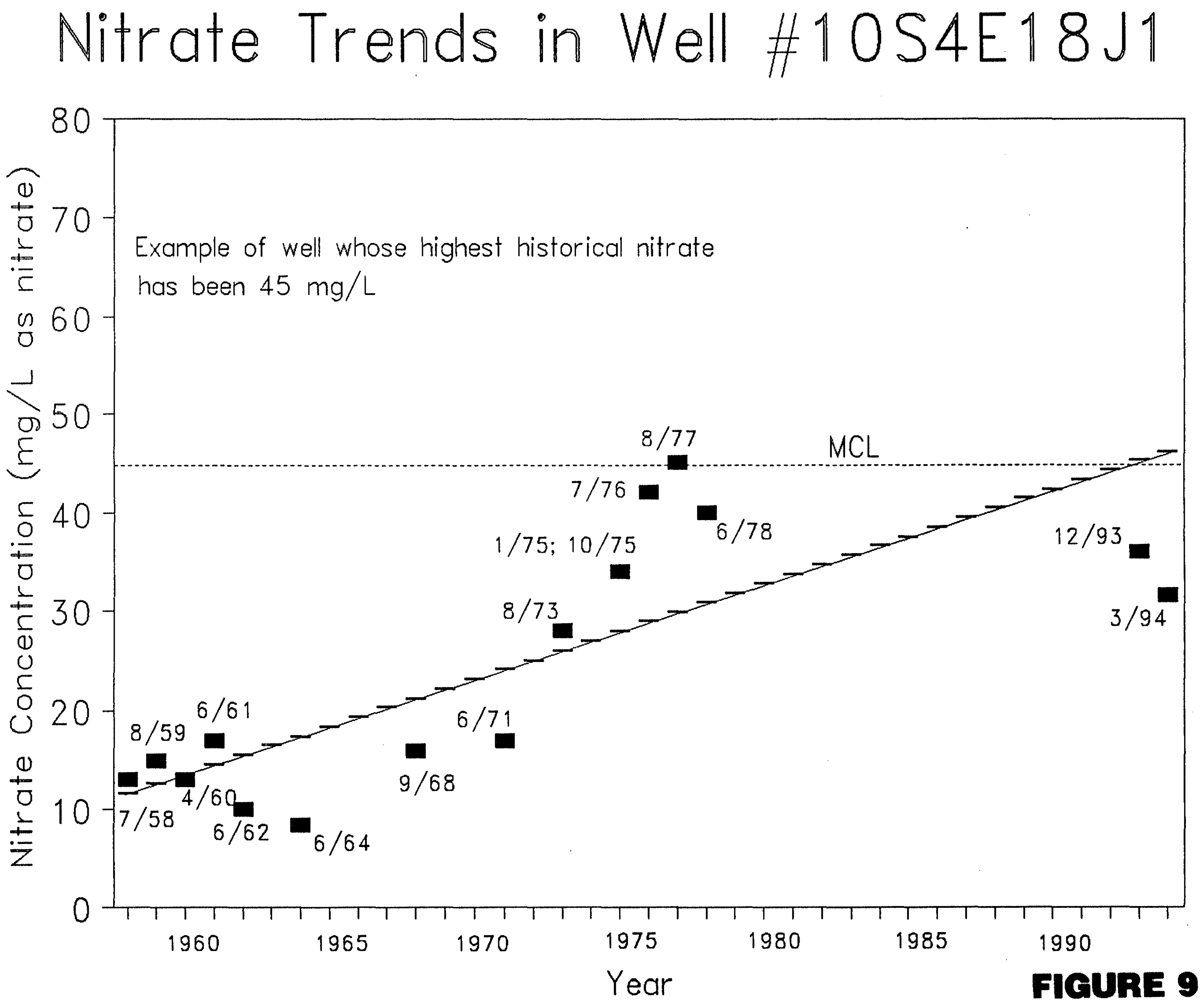


FIGURE 8



Nitrate Trends in Well #10S4E18J1
Example of well whose highest historical nitrate has been 45 mg/L
Nitrate Concentration (mg/L as nitrate)
0
10
20
30
40
50
60
70
80
MCL
8/77
7/76
6/78
1/75; 10/75
8/73
12/93
3/94
6/61
8/59
6/71
7/58
4/60
6/62
6/64
9/68
1960
1965
1970
1975
1980
1985
1990
Year

FIGURE 9

Nitrate Trends in Well #10S3E01E2

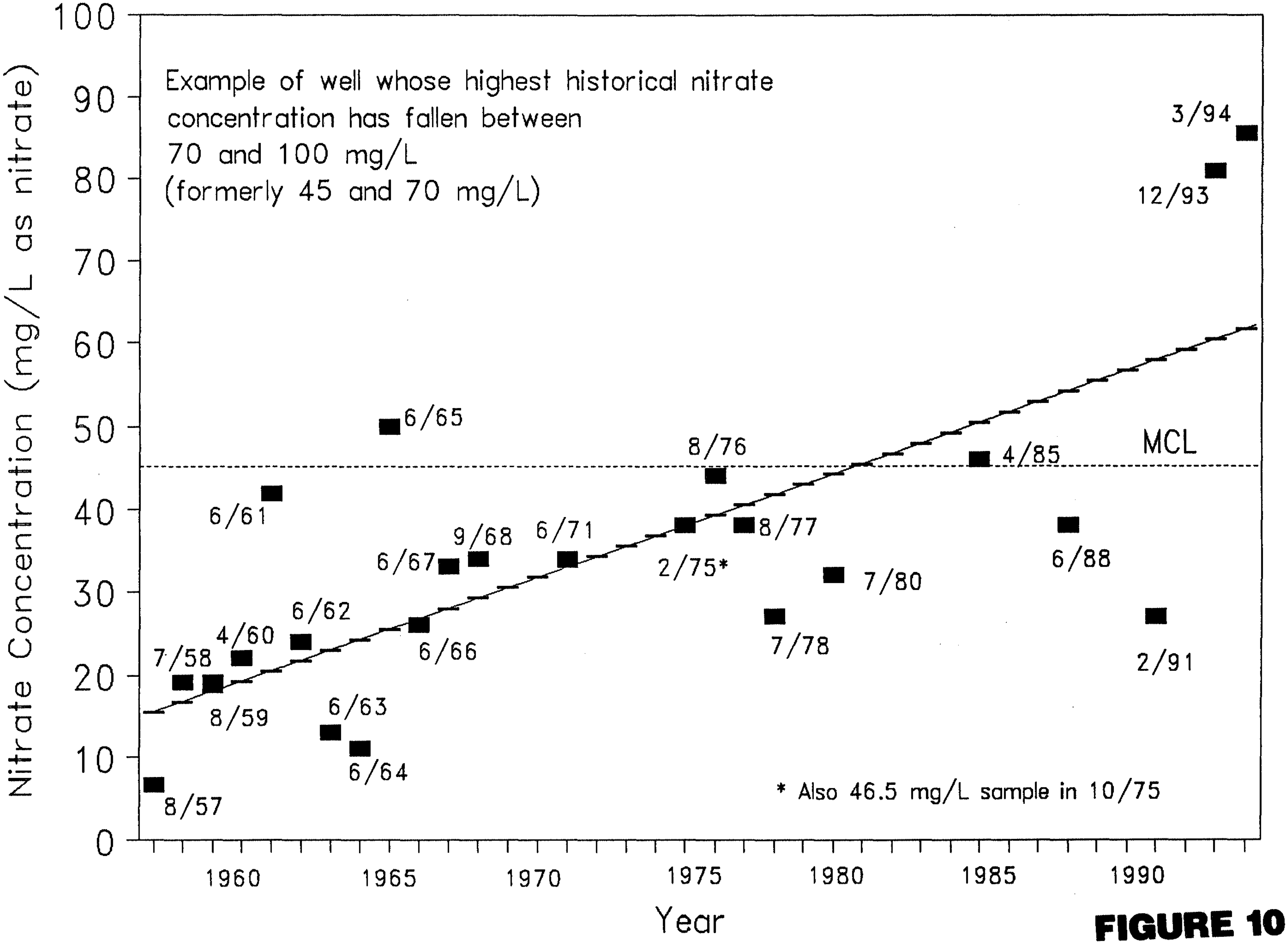


FIGURE 10

Nitrate Trends in Well #10S4E18G2

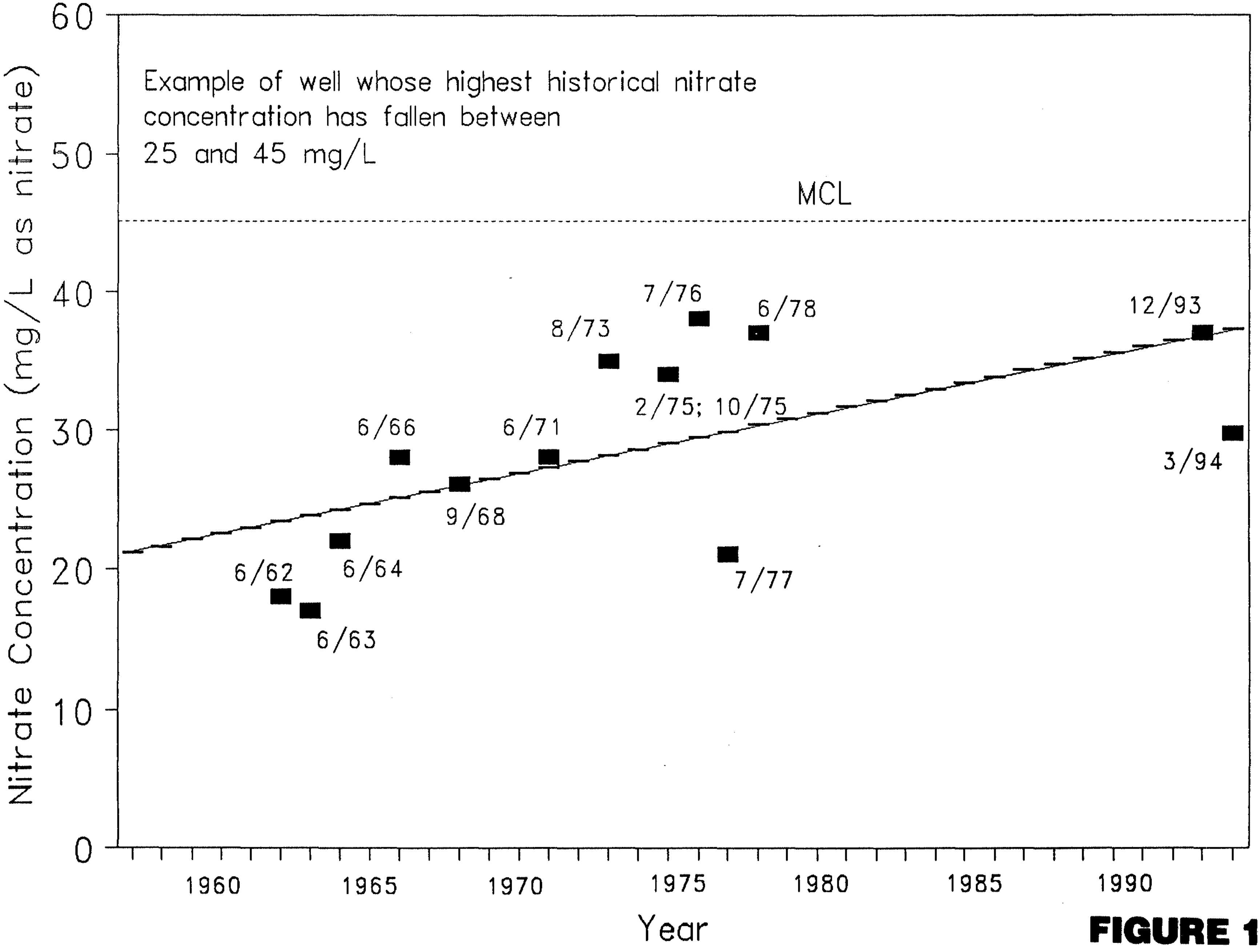


FIGURE 11

Nitrate Trends in Well #10S4E34L5

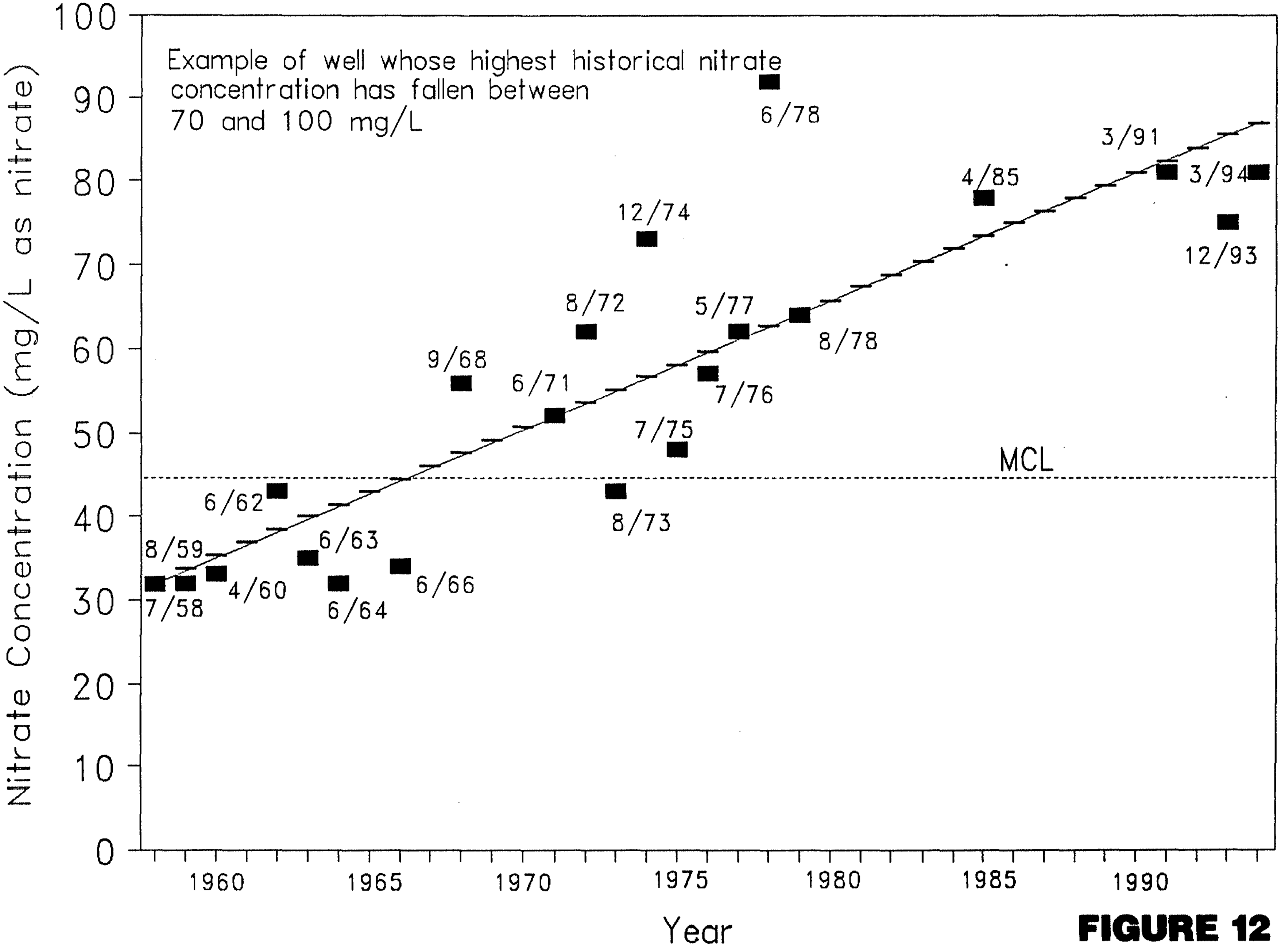
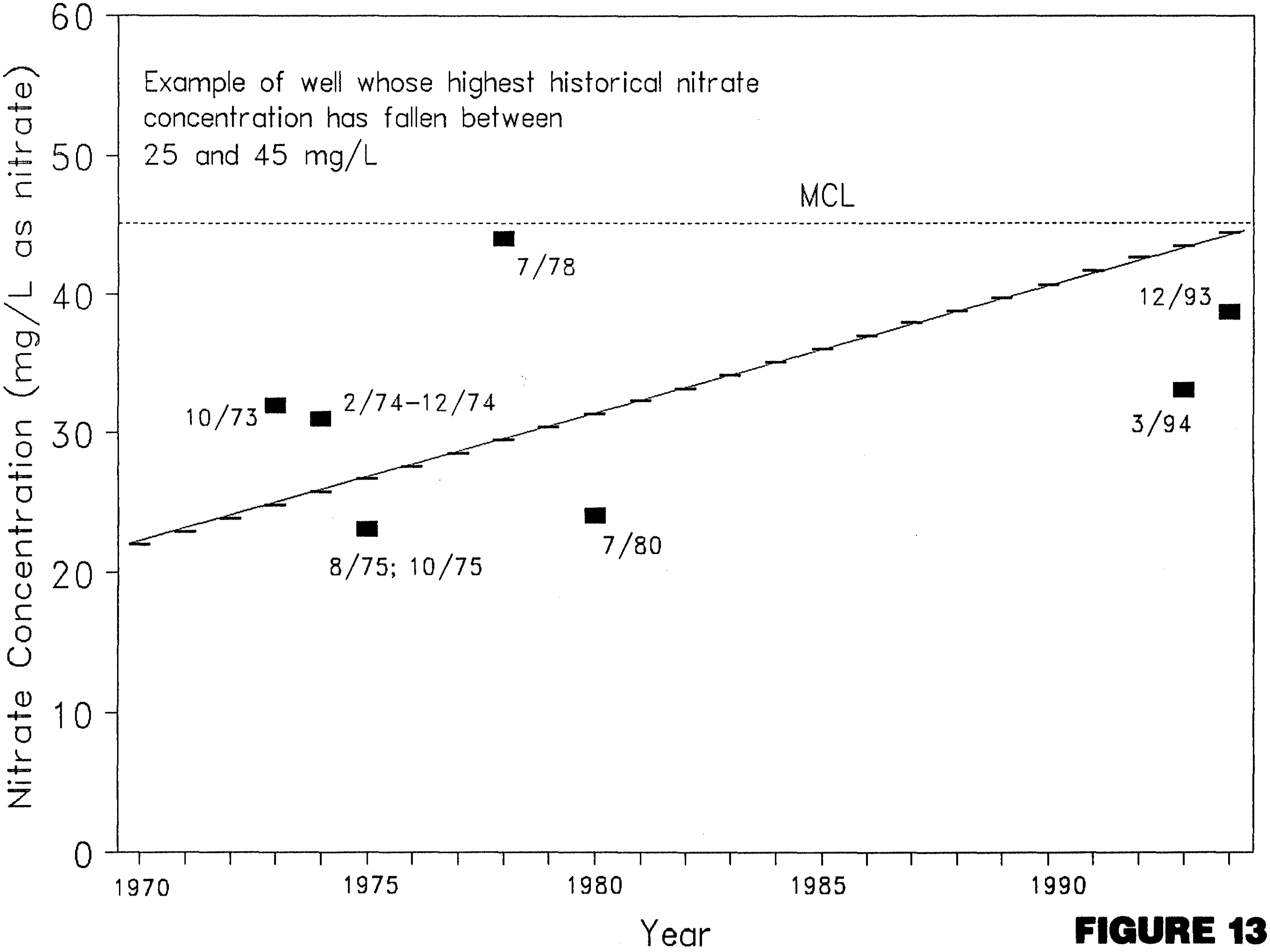


FIGURE 12

Nitrate Trends in Well #9S3E35D4



Example of well whose highest historical nitrate concentration has fallen between 25 and 45 mg/L

FIGURE 13

IX. NITRATES AND SOURCE AREAS

Wells were included in our sampling program for the purpose of monitoring groundwater quality in the vicinity of known nitrate sources. The full methodology of the selection process for these wells is outlined in the ``Sample Point Selection'' report; the primary selection factors included the distance between the source and the well, and the relative locations of the source and the well with respect to historical regional groundwater flow direction. The results of our sampling pointed out the limitations of our sampling program by providing results other than what we had anticipated.

Six point sources were selected for sampling areas, as indicated in Tables 1 and 2. A detailed discussion of nitrate sources in Llagas Basin can be found in our ``Nitrate Source Area Identification'' report. Two, and in one case, three, wells for each source were selected for sampling; one was located on the apparent upgradient side of the source, while one (or two) was located on the apparent downgradient side. In only one of six cases was the nitrate concentration in the apparent regional downgradient direction of the selected source higher than that of the upgradient well. This contradicted our expectations, which were that downgradient concentrations would be generally higher than upgradient concentrations. The fact that nitrate concentrations in wells located apparently upgradient from our sources were generally higher than apparently downgradient concentrations supports the need for additional field work and evaluations in order to fully study the relationship between nitrate concentrations in groundwater and point sources. The upgradient samples ranged from 21 to 99 mg/l of nitrate, and averaged 49 mg/l. The downgradient samples ranged from 15 to 34 mg/l and averaged 24 mg/l.

Other wells were selected to monitor groundwater in known land use areas which tend to produce nitrate, but do not contain point sources. The San Martin Special Use area was chosen for this purpose. Due to the density of potential nitrate sources, and to well sampling availability in this area, it was not possible to select diffuse nitrate source monitoring wells that were all ideally isolated. The results from these wells ranged from 19 to 68 mg/l and averaged 31 mg/l. Two of these wells are located along the northern edge of San Martin, regionally upgradient of all the point sources considered in our study. These may be the samples most representative of groundwater affected by the San Martin Special Use area. Samples collected from these wells ranged from 28 to 68 mg/l, and averaged 47 mg/l. The detection of nitrate contamination in these two wells, along with similar levels of nitrates found in the nearby ``trend'' well, may indicate that the San Martin Special Use area is a diffuse source of nitrates affecting groundwater. Without complete knowledge of the nearby historical land uses, however, this cannot be a firm conclusion.

CONSIDERATIONS

The results of our source vicinity sampling illustrate three main points to consider when reviewing our data, as follows:

Without a detailed hydrogeologic evaluation of each source area under study, it may be unwise to assume that a ``downgradient'' well is truly the best location to monitor the groundwater potentially affected by a nitrate source. Although regional groundwater data indicate that groundwater flows from a source towards a ``downgradient'' water well, other hydrogeologic and physical features may dictate that nitrate from a source travels in a different direction. The groundwater flow directions in the immediate source areas may or may not agree with the general flow direction in Llagas Basin. Also, features affecting the migration of nitrate may include abandoned wells, local pumping conditions, discontinuous impermeable layers, preferential migratory pathways, perched water zones, and others. The deeper the zone of completion of a well, the lower the chance that the well is monitoring a zone affected only by the land use immediately above it. Nitrates can move in relation to local influences rather than regional flow direction as represented on available maps.

Another reason that our downgradient samples generally revealed lower nitrate concentrations than did our upgradient samples may be related to when the most significant nitrate discharge from the source occurred. If the highest nitrogen loading from the selected sources occurred decades ago, it may be the case that the area of highest contamination has already passed what we selected as a downgradient well. The upgradient wells we selected may in fact be distant downgradient wells for other nitrate sources.

Superposition of sources should also be considered in Llagas Basin. Not only are the sources we selected located in close proximity to each other, but other historic sources which were not considered when selecting our sampling points likely exist. Any water well in the area is potentially affected by multiple point and non-point sources. Without detailed hydrogeologic knowledge and an exhaustive history of land uses in the subject area, it is difficult to say that one water well is only influenced by one facility.

X. SUPPLEMENTARY ANALYTES

The groundwater samples collected during this phase of the nitrate study were analyzed for several analytes in addition to nitrate. Although nitrate is the main form of nitrogen in which nitrate occurs in groundwater (Freeze and Cherry, 1979, p. 413), the analysis of other nitrogenous compounds along with other parameters may offer insight into sources of nitrate. The non-nitrate data collected during this study may be fully used in more detailed studies in the future. The following paragraphs briefly discuss the reasons for choosing each analyte and the results from our sampling.

CHLORIDE

Correlations between chloride and nitrate occurrence in groundwater basins have been demonstrated (Saffigna and Keeney, 1977). Chloride occurrence in groundwater has been associated with various sources, including septic systems (Alhajjar, 1990; Rolston et al., 1994a, p. 31), and potassium chloride fertilizer (Saffigna and Keeney, 1977). Chloride, like nitrate, is known to act as a tracer contaminant, travelling readily with groundwater through the subsurface.

Chloride concentrations detected in samples from our wells were plotted against the corresponding nitrate concentrations. Please refer to Figure 14. No correlation between the two parameters was evident. This is also apparent from inspecting the map of chloride concentrations in Figure 15; the wells producing water with the highest chloride concentrations did not, in general, produce water with the highest nitrate concentrations. Similarly, a negative correlation between the two parameters is not shown by the data. Chloride/nitrate ratios in other study areas have been consistent; strong positive correlations between the two have been demonstrated in agricultural areas (Saffigna and Keeney, 1977) and septic tank areas (Rolston et al., 1994a, p. 31).

Our sampling results suggest that nitrates and chlorides in the basin do not have the same major source(s). However, suspected sources of both chloride and nitrate, such as septic tanks and fertilizers, cannot be ruled out as nitrate sources, as the percent contribution of chloride from each suspected nitrate source has not been investigated, and other chloride sources may exist. There is no known major naturally occurring source of chlorides, such as evaporites or connate waters, in Llagas Basin. Additionally, the patterns of non-chloride and chloride based fertilizers in the study area has not been thoroughly investigated. It is beyond the scope of this study to fully investigate the occurrence of chloride in Llagas Basin.

NITRITE, AMMONIA, AND TOTAL KJELDAHL NITROGEN

Other nitrogenous analytes were included in our sampling program. These included nitrite, ammonia, and TKN. As discussed below, these analytes were not expected to be detected in Llagas Basin groundwater, and our findings generally support this hypothesis.

Nitrite is a transitory product of the nitrification process, and as such, is expected only in low or non-existent concentrations in groundwater. Concentrations of nitrite in groundwater systems are usually less than 0.1 mg/l and rarely greater than 1 mg/l (Sawyer and McCarty, 1978, pg. 450; Klein and Bradford, 1980). Figure 16 illustrates nitrite distribution in this study area.

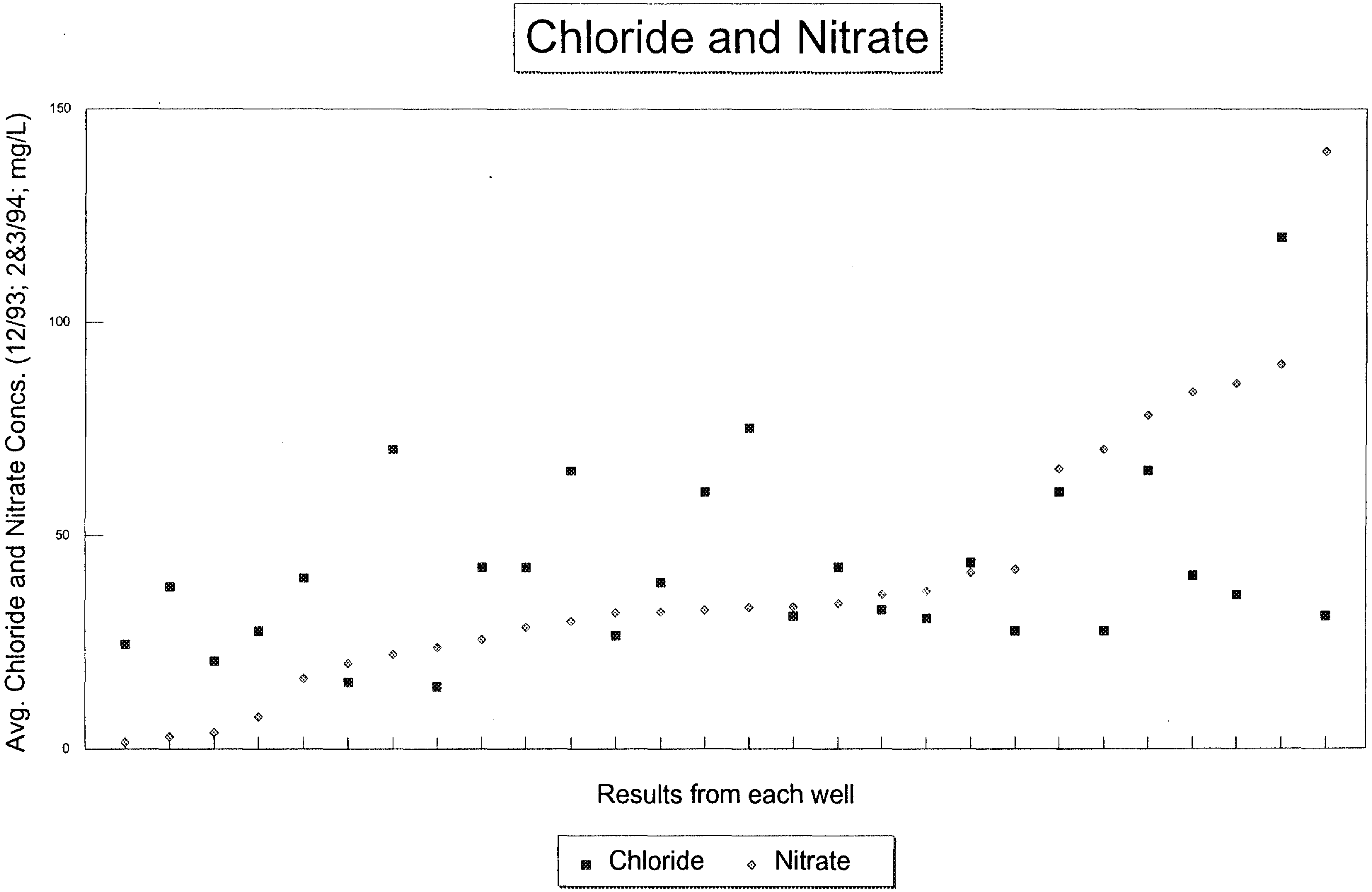

Chloride and Nitrate
150
100
50
0
Avg. Chloride and Nitrate Concs. (12/93; 2&3/94; mg/L)
Results from each well
▨ Chloride
◇ Nitrate

FIGURE 14

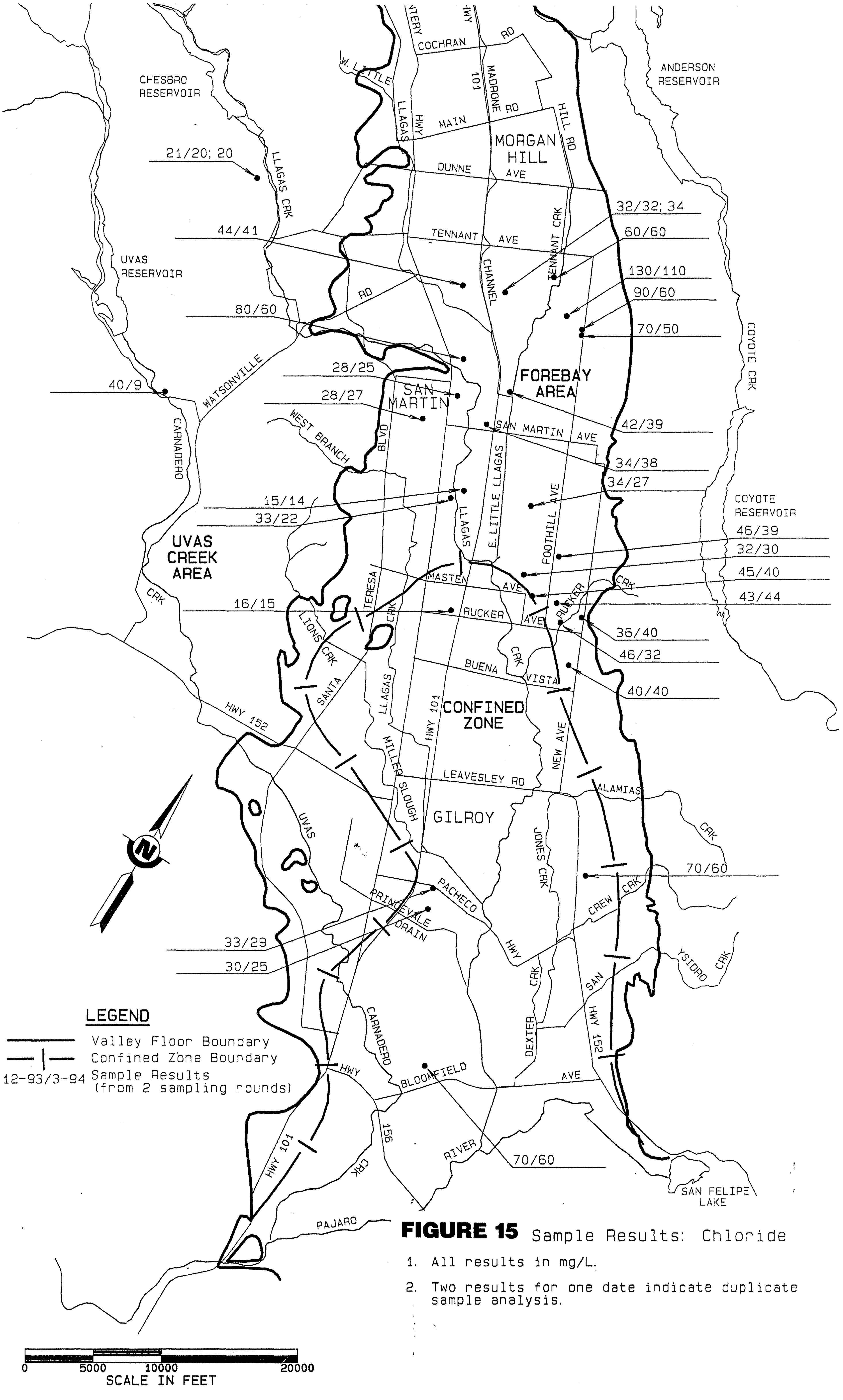


FIGURE 15 Sample Results: Chloride

1. All results in mg/L.
2. Two results for one date indicate duplicate sample analysis.

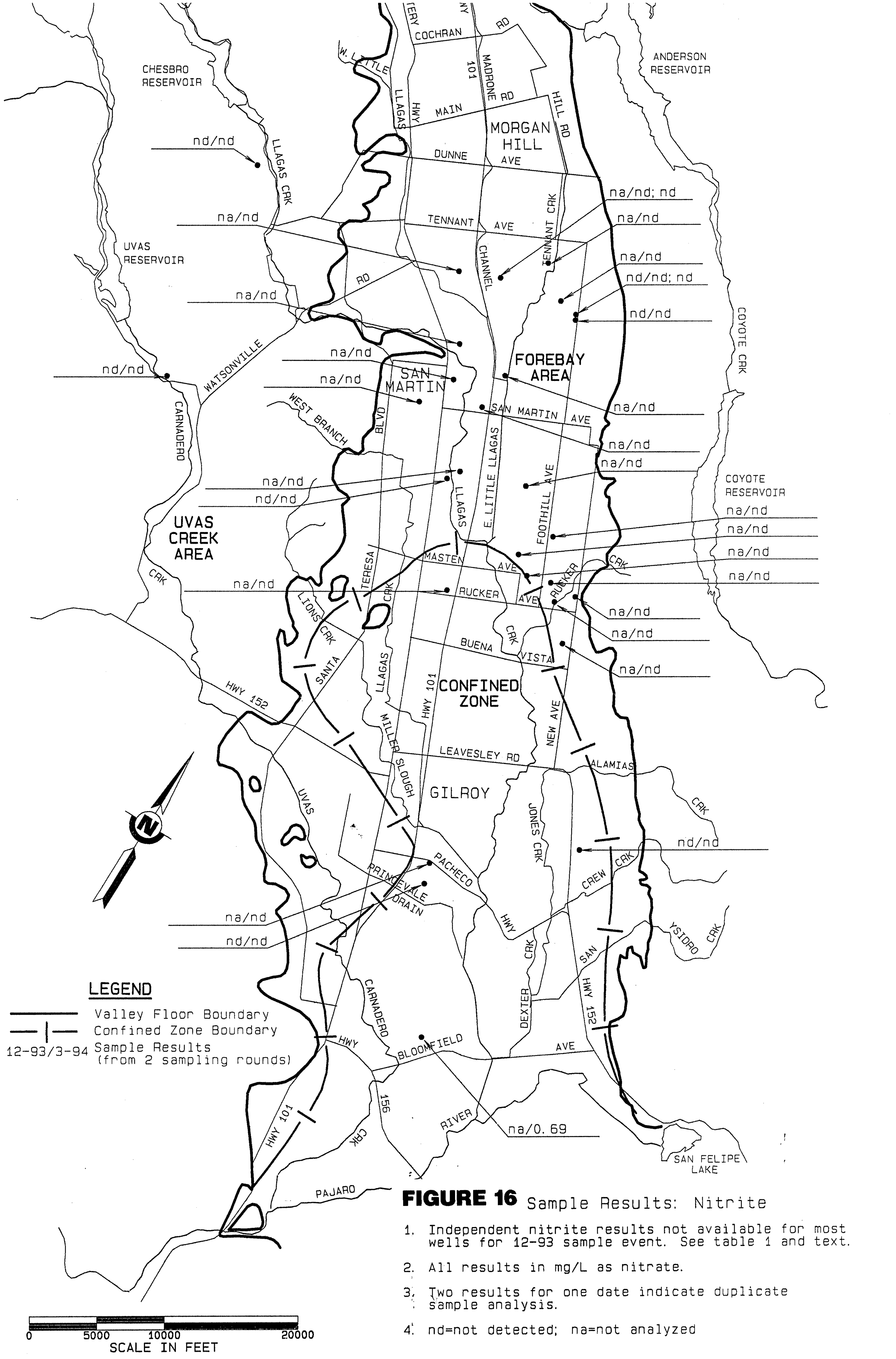


FIGURE 16 Sample Results: Nitrite

1. Independent nitrite results not available for most wells for 12-93 sample event. See table 1 and text.
2. All results in mg/L as nitrate.
3. Two results for one date indicate duplicate sample analysis.
4. nd=not detected; na=not analyzed

Nitrite as an independent analyte was included on seven occasions during the December 1993 sampling and for every well during the February/March 1994 sampling event. In only one instance was a concentration above the detection limit found. This trace amount, 0.21 mg/l as nitrogen, was found in water from well No. 11S/04E-16R02, located generally south of the Gilroy-Morgan Hill Municipal Wastewater Facility. It is likely that this is an anomalous result, as all nitrite is expected to be fully nitrified before reaching the saturated zone. However, the finding could be an indication that wastewater plant effluent is short-circuiting to local groundwater. Typical nitrite levels in plant effluent range from .31 to .50 mg/l (Slechta, Al, Gilroy-Morgan Hill Municipal Wastewater Facility, personal communication, 1993). Nitrite has also been detected in similar concentrations in groundwater samples collected from shallow monitoring wells at the plant (CRWQCB, 1994). A direct hydraulic connection that does not provide the nitrite adequate time to nitrify is unlikely, however, especially since the gravel pack for the water well sampled in our study is reported to start at 96 feet below ground surface.

TKN is a measurement of organic and ammonia nitrogen. If detected in groundwater, it is expected to be in much lower concentrations than nitrate (Freeze and Cherry, 1979, p. 442). Organic nitrogen may be converted to ammonia through mineralization. Through nitrification, ammonia can be oxidized to nitrite, and finally nitrate, the generally stable form of dissolved nitrogen in groundwater. The processes of mineralization and nitrification have generally converted nitrogenous compounds to nitrate before they can be transported with groundwater. Like nitrite, TKN was only detected in one instance during our sampling program. This detection was in water from well No. 10S/03E-18J01, located away from the valley floor of the study area. The detection may be an anomaly; however, it is not unreasonable that TKN was detected in this well. Away from the valley floor, the well is probably fairly shallow and may be susceptible to direct infiltration from surface nitrogen sources. Concentrations of TKN in Gilroy Waste Water Plant effluent, for example, have been reported in the 30's of mg/l (Slechta, personal communication, 1993). Shallow monitoring wells at the plant have recently produced water containing TKN in concentrations as high as 5.9 mg/l (CRWQCB, 1994). TKN was not detected in our study's two southernmost wells, lending support to the argument that organic nitrogen in that area is ammonified and/or nitrified before reaching deeper groundwater, away from the immediate vicinity of the plant. Please refer to Figure 17.

Like nitrite and TKN, ammonia is not expected in significant quantities in groundwater (Klein and Bradford, 1980). This was confirmed by our sampling program, which revealed no detectable concentrations of ammonia in any of the samples for which it was analyzed. Please see Figure 18.

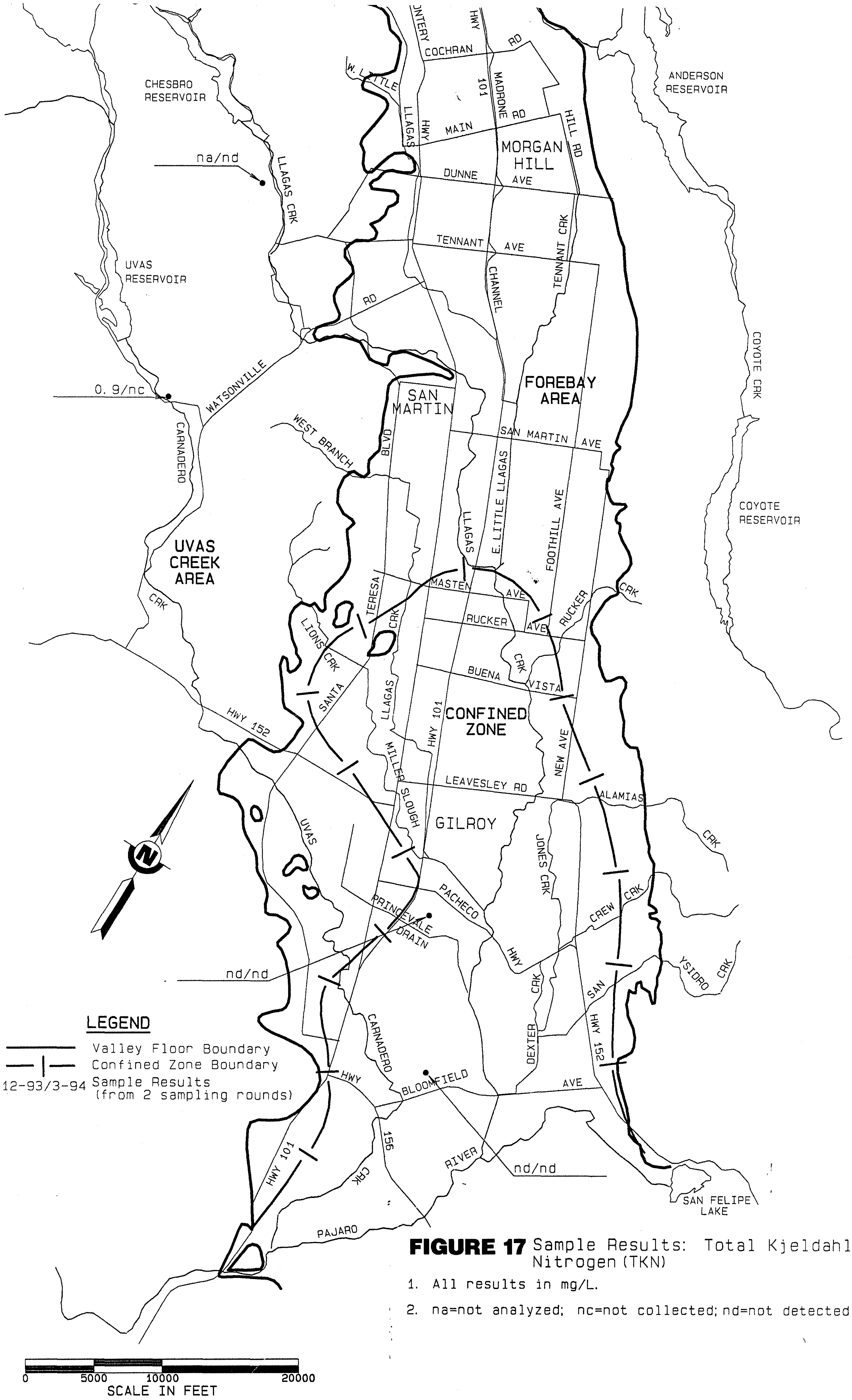


FIGURE 17 Sample Results: Total Kjeldahl Nitrogen (TKN)

1. All results in mg/L.

2. na=not analyzed; nc=not collected; nd=not detected

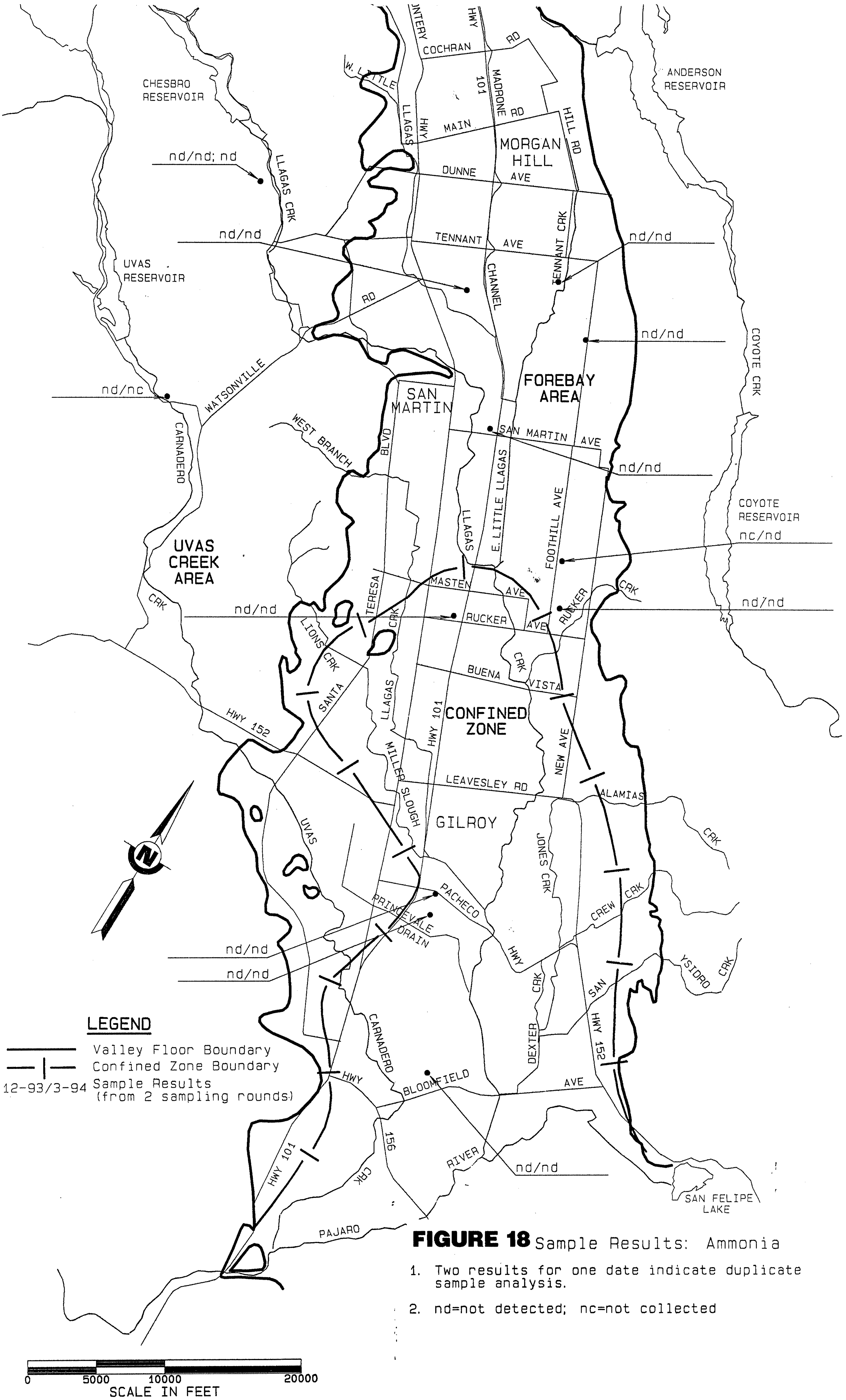


FIGURE 18 Sample Results: Ammonia

1. Two results for one date indicate duplicate sample analysis.
2. nd=not detected; nc=not collected

STABLE OXYGEN ISOTOPE RATIO

Previous studies have used $\delta^{18}O$(7) values in groundwater characterization studies (Mohr, et al., 1992; Aravena, et al., 1993; Davisson and Criss, 1993). We plotted these stable isotope values against nitrate concentrations for each well and found no correlation. Please refer to Figure 19. This may indicate that nitrate is present in both relatively young and old groundwaters in the basin, as $\delta^{18}O$ values are often indicators of the amount of time groundwater has spent in contact with the aquifer formation. The $\delta^{18}O$ distribution in the study area is shown in Figure 20.

DISSOLVED OXYGEN

Dissolved oxygen was included in our sampling program since it is easily measured in the field. Please see Figure 21. Elevated dissolved oxygen concentrations may indicate that groundwater is receiving direct recharge from surface waters. The dissolved oxygen concentrations observed during our sampling events varied from near zero to values above the usual saturation concentration. In general, the values were higher than one would expect from water supply wells; this may indicate that many wells may be directly influenced by surface water. In recharge areas with sandy or gravelly soil, shallow groundwater commonly contains detectable dissolved oxygen, greater than about 0.1 mg/l. In recharge areas with silty or clayey soils, shallow groundwater commonly does not contain detectable dissolved oxygen. Dissolved oxygen content generally decreases as water percolates through the subsurface (Freeze and Cherry, 1979, p. 245). Our dissolved oxygen concentrations did not correlate with well depth or depth of screened interval. Dissolved oxygen readings were collected from water after significant purging of each well, to be representative of the water sent to the laboratory for chemical analysis. During pumping and atmospheric exposure, oxygen may become entrained in groundwater and have led to results not representative of in-situ conditions. Due to the wide range and high values of dissolved oxygen concentrations in our samples, and due to sampling methods, we do not believe the dissolved oxygen readings are representative of dissolved oxygen concentrations in the water-bearing zones that our wells intercept.

STABLE NITROGEN ISOTOPE RATIO

Values of $\delta^{15}N$(8) have also been used in groundwater nitrate investigations; numerous references are available in Rolston, et al., 1994. ``The need for sound hydrologic characterizations of the subsurface

---

[7] The ^{18}O concentrations of water are expressed as per mil (‰) differences relative to Standard Mean Ocean Water (SMOW), a laboratory standard maintained by the National Bureau of Standards. The values are reported in the usual δ notation such that:

$$\delta = \left(\frac{R}{R_{std}} - 1\right) x\ 1000$$

where R is the $^{18}O/^{16}O$ ratio of a sample, and R_{std} represents $^{18}O/^{16}O$ ratio of SMOW (Mohr, et al, 1992)

[8] The $\delta^{15}N$ value is derived using the following equation:

$$\delta^{15}N\ (ppt) = \frac{(^{15}N/^{14}N)\ sample\ -\ (^{15}N/^{14}N)\ standard}{(^{15}N\ /^{14}N)\ standard}\ x\ 1000$$

The $(^{15}N/^{14}N)$ standard is the $^{15}N/^{14}N$ ratio of the atmosphere (Rolston et al, 1994a, Appendix I, p. 25).

is an inescapable fact in (nitrate) source investigations (Rolston, et al., 1994, p. 76)." The report stresses that $\delta^{15}N$ values alone are not sufficient to identify specific nitrate sources: ``The chief weaknesses of the $\delta^{15}N$ approach are that the $\delta^{15}N$ signature can represent an unknown mixture of different sources and the signature by itself says nothing about location of the source(s) with respect to the observed contamination. Additionally, the $\delta^{15}N$ technique appears ineffective for distinguishing manufactured fertilizer sources from naturally occurring soil organic matter sources. Significant denitrification within the profile would tend to increase the $\delta^{15}N$ values above that of the source (p. 74)." The scope of our study did not allow for the collection of detailed hydrogeologic information and vadose zone sampling results for our selected source sampling areas. Therefore, definitive conclusions about the precise source(s) of nitrate in our selected wells could not be made. Also, a correlation between $\delta^{15}N$ values and nitrate concentrations in our data was not evident. A similar lack of correlation between $\delta^{15}N$ values and chloride concentrations was noted. Please refer to Figures 22 and 23. The report also illustrates reported ranges of $\delta^{15}N$ values for various nitrate sources reported in previous literature. Discounting results from samples collected on March 2, 1994 and March 7, 1994, the $\delta^{15}N$ values from our study's samples from both sampling rounds ranged from -1.89 to +8.40; the average of these samples was +2.27. Please see Figure 24 for $\delta^{15}N$ distribution in the study area.

The range of isotope values in all our wells allows us to draw some conclusions regarding the types of nitrate sources in Llagas Basin. It appears that animal waste and sewage are not the principal nitrate contributors. These sources usually have $\delta^{15}N$ values of +10 to +20 (Rolston, et al., 1994a, Appendix I, p. 29). Our samples only ranged to +8.4; only two wells produced groundwater with $\delta^{15}N$ values in excess of +5. Ninety percent of fertilizer $\delta^{15}N$ values fall within the -3 to +2 range. Since the primary mechanism for isotope value alteration once nitrogen has been converted to nitrate is denitrification, which only increases isotope ratios, animal/sewage wastes would not exhibit isotope values as low as those seen in our sampling program. It is possible that groundwater with high $\delta^{15}N$ readings has blended with groundwater with low $\delta^{15}N$ readings before being pumped from the wells in our sampling program. However, several wells in our study were only screened in a particular deep or shallow zone, and none of these produced water with high enough $\delta^{15}N$ values to be representative of an animal waste or sewage source.

Nitrogen from rainwater and soil organic nitrogen appear to be of secondary importance. As previously explained, significant nitrate contamination was discovered in groundwater from the two shallow monitoring wells in our program. Since we are reasonably confident that these wells are producing water from their reported screening depths, and since shallow groundwater has not yet mixed with water in deeper zones, we performed a more detailed source identification exercise for the nitrate contamination in these wells.

Discounting the second round $\delta^{15}N$ results for reasons previously explained, the $\delta^{15}N$ values for our two shallow wells were +0.14 and -0.38. These stable isotope values are in general agreement with those reported in the literature for nitrogen from rainfall and fertilizer (Rolston et al., 1994a, Appendix I, p. 31). Nitrates from animal or human waste usually have $\delta^{15}N$ values above +10 (Rolston, et al., 1994a, Appendix I, p. 29) and can be ruled out as discussed in more detail above. Typical soil organic nitrogen values, ranging from +2 to +8 in the literature, are closer to those in our shallow groundwater samples, (Rolston, et al., 1994a, Appendix I, p. 28). However, after initial cultivation in an area, soil organic nitrogen is initially depleted, and represents only less than 1 percent of the nitrogen from fertilizer (Rolston et al, 1994a, Appendix I, p. 34). This argument is more valid in areas where shallow groundwater is sampled, as the time lag between land use changes (i.e., start of cultivation) and groundwater nitrate concentration fluctuation is reduced.

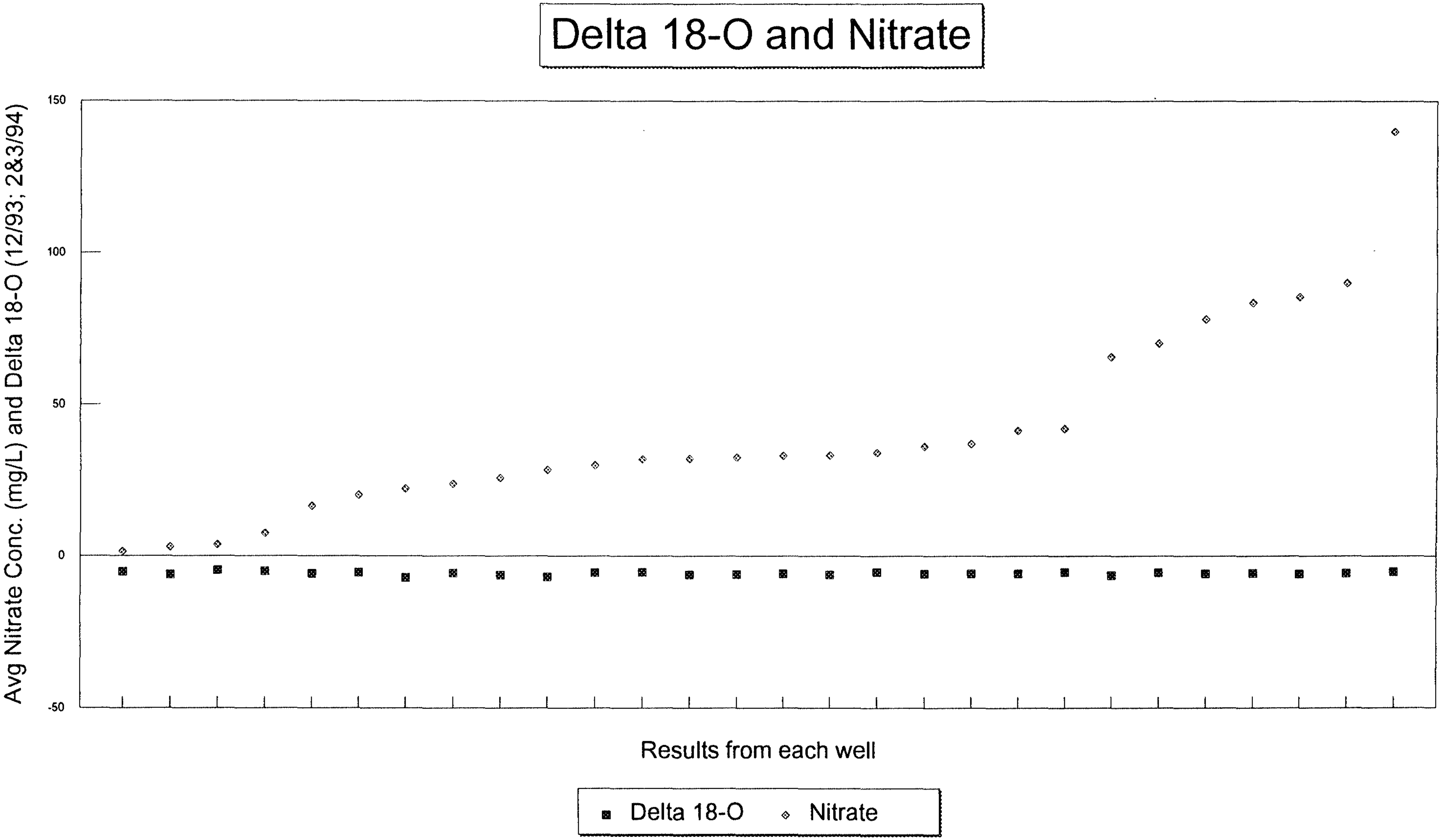

Delta 18-O and Nitrate
Avg Nitrate Conc. (mg/L) and Delta 18-O (12/93; 2&3/94)
150
100
50
0
-50
Results from each well
Delta 18-O
Nitrate

FIGURE 19

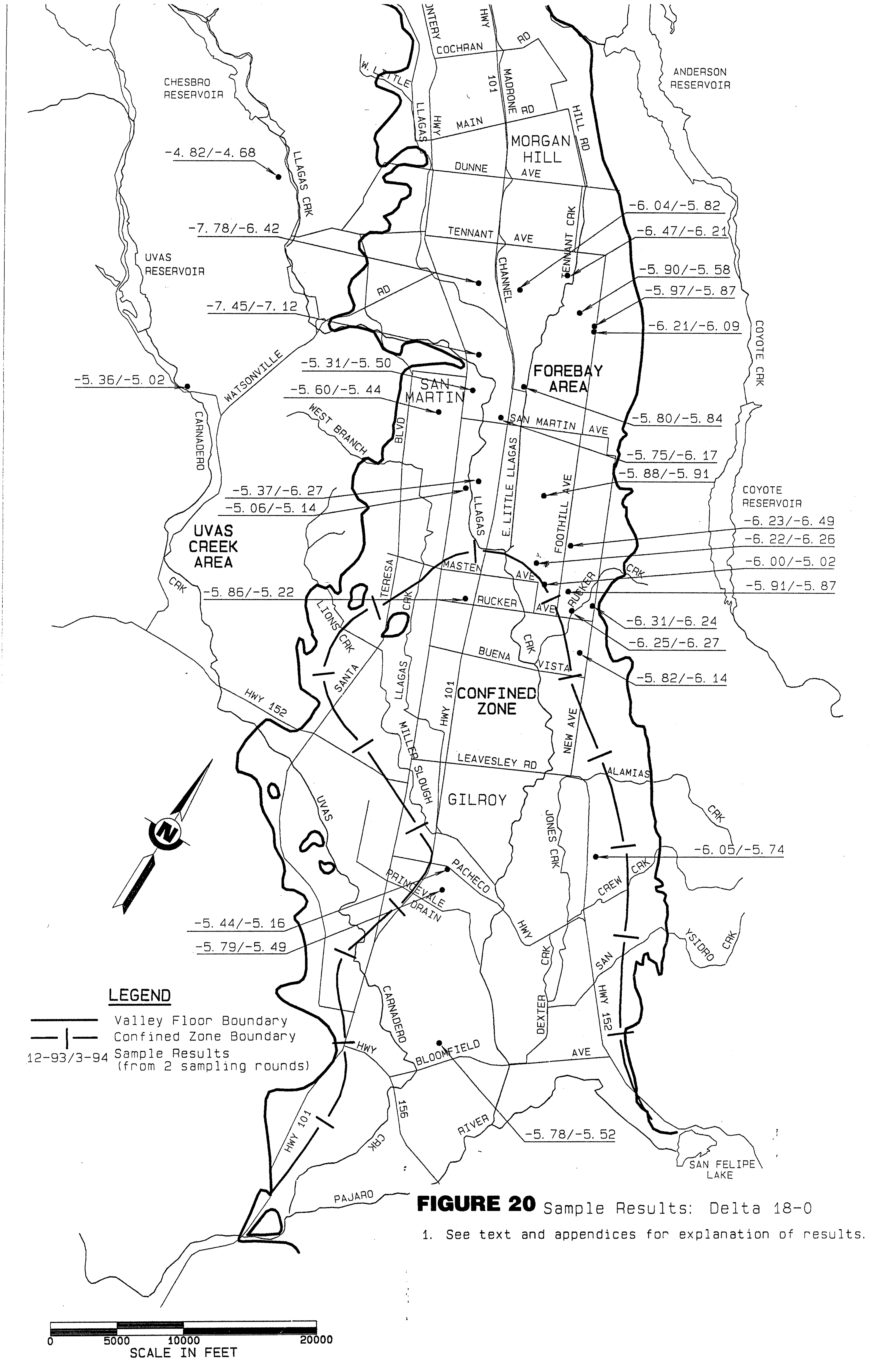


FIGURE 20 Sample Results: Delta 18-0

1. See text and appendices for explanation of results.

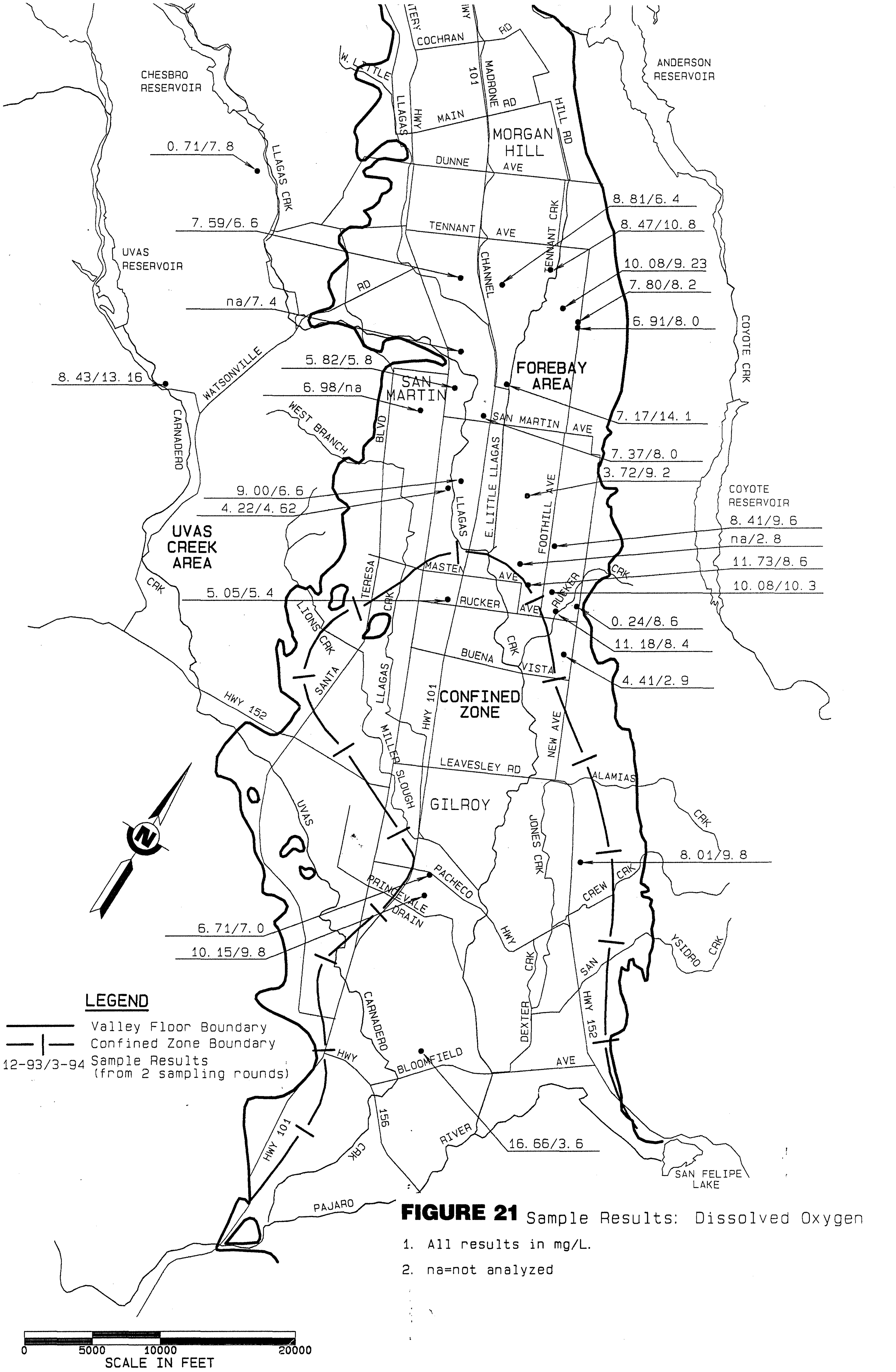


FIGURE 21 Sample Results: Dissolved Oxygen

1. All results in mg/L.
2. na=not analyzed

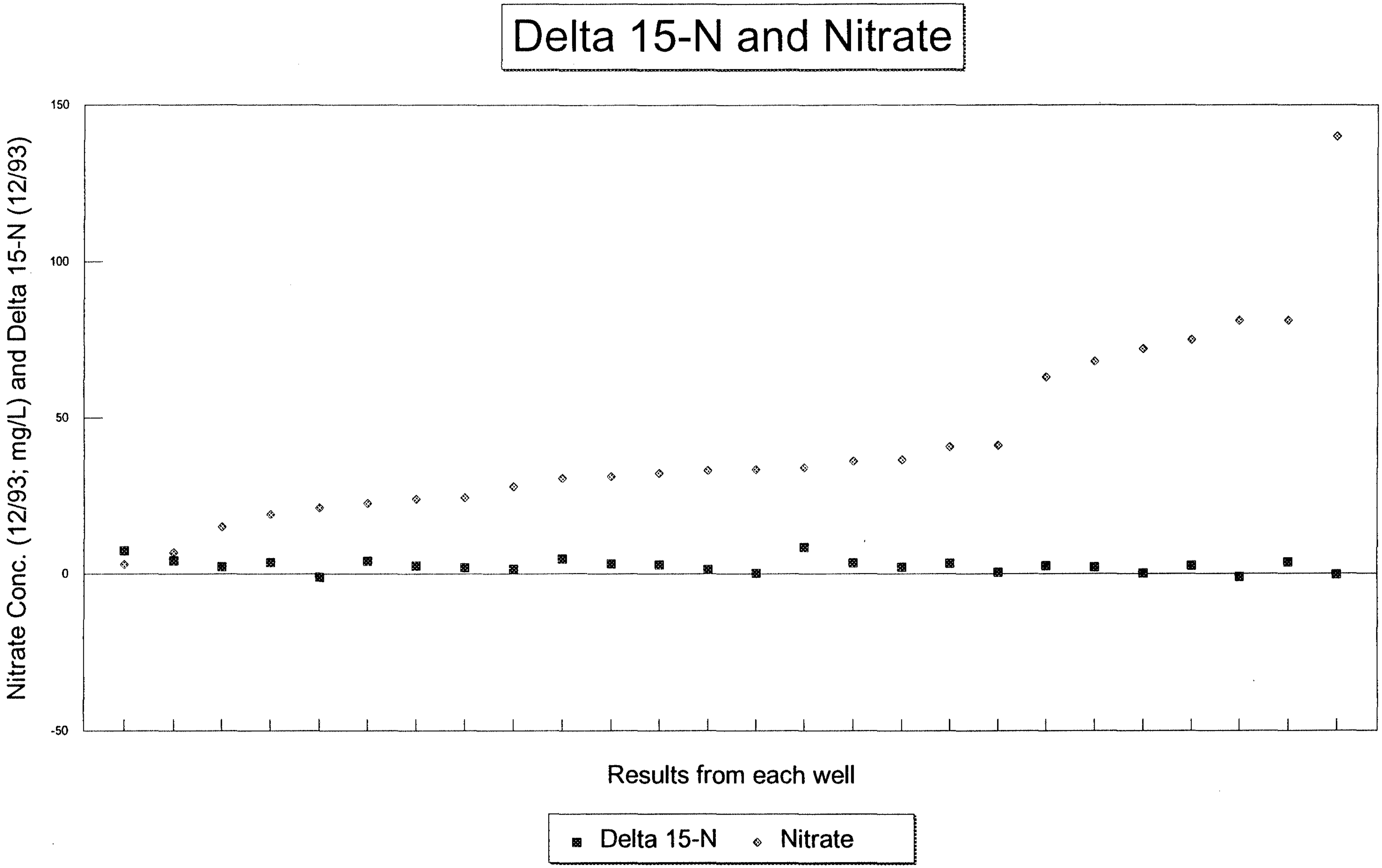
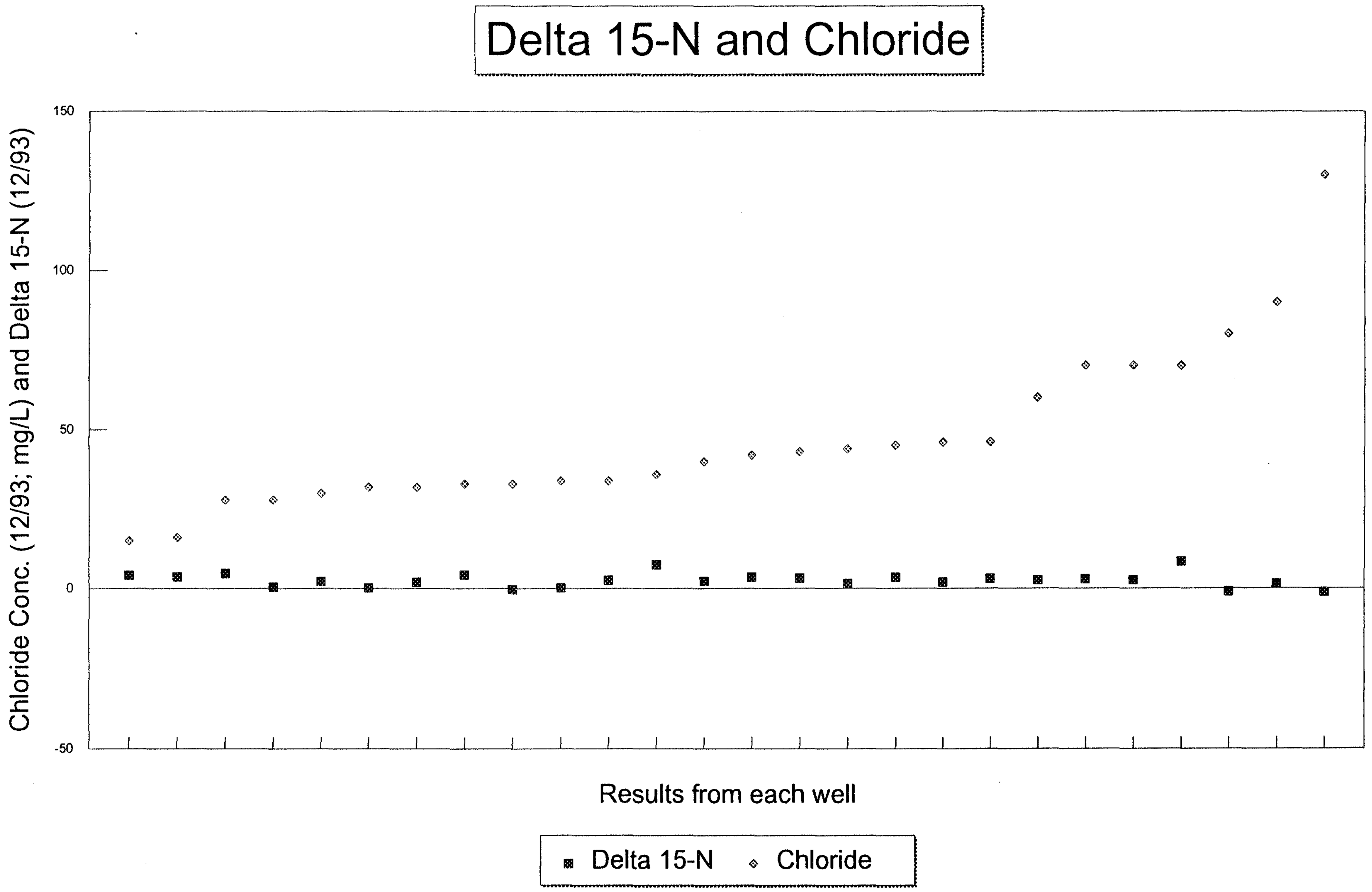

Delta 15-N and Nitrate
150
100
50
0
-50
Nitrate Conc. (12/93; mg/L) and Delta 15-N (12/93)
Results from each well
Delta 15-N
Nitrate

FIGURE 22



Delta 15-N and Chloride
150
100
50
0
-50
Chloride Conc. (12/93; mg/L) and Delta 15-N (12/93)
Results from each well
▨ Delta 15-N
◇ Chloride

FIGURE 23

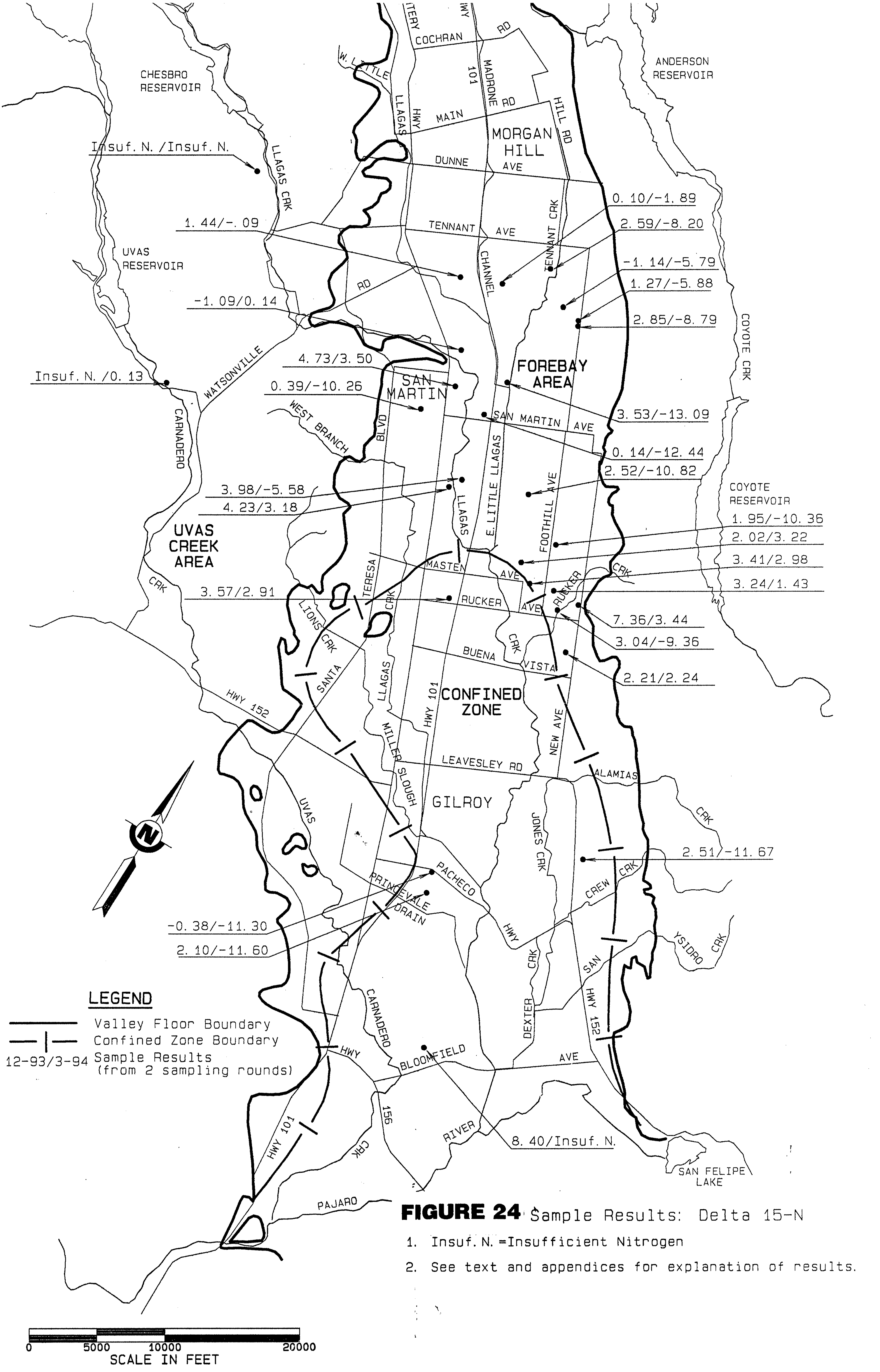


FIGURE 24 Sample Results: Delta 15-N

1. Insuf. N. =Insufficient Nitrogen
2. See text and appendices for explanation of results.

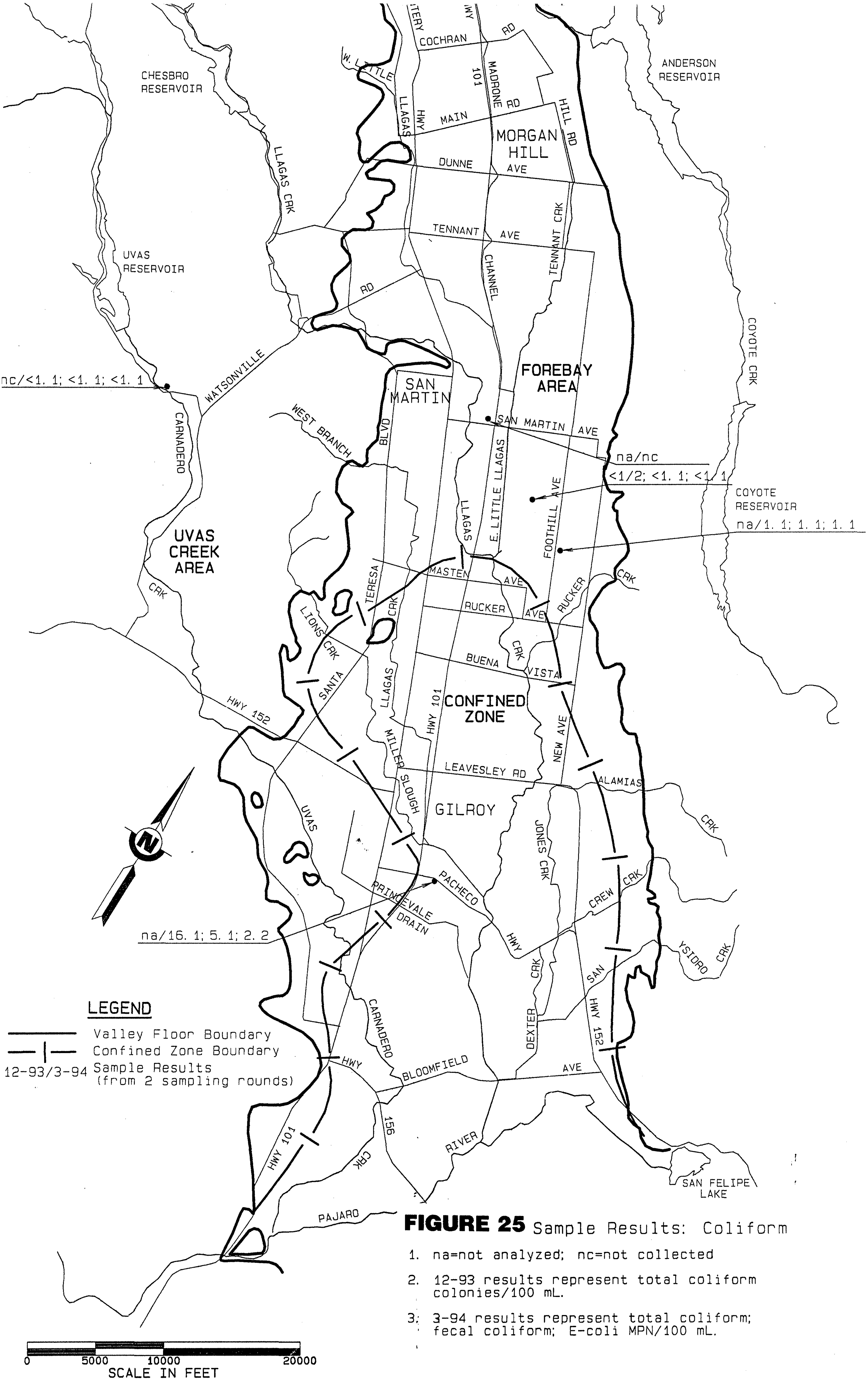


FIGURE 25 Sample Results: Coliform

1. na=not analyzed; nc=not collected
2. 12-93 results represent total coliform colonies/100 mL.
3. 3-94 results represent total coliform; fecal coliform; E-coli MPN/100 mL.

XI. CONCLUSIONS

We were able to draw several primary conclusions from the data collected during the sample collection phase of the study. The data we collected was reviewed in conjunction with historical nitrate results and nitrate source information from the study area. It is important to note that significant limitations were encountered during our study which preclude us from making certain conclusions. These limitations include the lack of source site-specific geologic data and the absence of soil water quality data. Although these factors prevented us from correlating well water nitrate concentrations with specific nitrate sources, we were able to draw some meaningful conclusions regarding the occurrence and sources of nitrates in Llagas Basin. These conclusions as well as our conclusions regarding the areal and vertical distribution of nitrates and nitrate trends in the study area are summarized below.

Consistent with conclusions drawn in our ``Nitrate Data Review'' report dated August 1993, our sampling program confirmed the presence of localized instances of nitrate contamination located throughout Llagas Basin. This does not imply that the entire groundwater basin is contaminated with nitrates, but does indicate that nitrate occurrence is not restricted to any particular location in the study area. Also, the sampling results for this study were consistent with historical data in showing that the southern portion of the study area appears to contain a higher percentage of water wells producing water with nitrate contamination in concentrations significantly exceeding MCLs than does the northern portion.

Nitrate appears to be present at all depths to which the wells used were screened. Water collected from the two wells screened in the shallow zone contained high concentrations of nitrates. Nitrate above MCLs was also discovered in wells reportedly screened in only a deep water bearing zone. Depth-specific nitrate profiles were not developed, due to the limited number of aquifer-specific monitoring wells. However, we did plot nitrate concentrations versus top and midpoint of the reported screen interval as well as nitrate concentrations versus total well depth. A loose correlation indicating that nitrate concentrations decrease with perforated interval was evident.

In general, our sampling data supported the generally increasing trend of nitrates seen in our historical data review; the results fell within the ranges of historical data. When evaluating the data in more detail, nitrate concentration trends in our selected wells did vary however. Sampling results from half of the wells clearly showed a generally increasing trend. Samples from one ``example'' well were much higher than previously observed concentrations, while nitrate concentrations from two other wells were below the trend expected when extrapolating from historical data. Trends seen in these wells are not necessarily representative of nitrate trends throughout the study area.

Comparison of results from the trend wells with results from other nearby wells helps to confirm the hypothesis that nitrate occurs in Llagas Basin in numerous localized areas, rather than throughout the entire basin. A review of Figure 4 shows that wells producing water with high nitrate concentrations are often situated relatively close to those producing less contaminated water. ``Plumes'' or large areal extents of nitrate-contaminated groundwater are not evident from our recent sampling data, or from historical data. Nitrate contamination in the study area likely exists in numerous localized, and possibly transient, ``hot'' spots, rather than basin wide. Sources which contribute nitrate on an intermittent basis may create this phenomenon. The wells used in our sampling program are likely completed in just a fraction of those localized high nitrate concentration areas.

The supplementary analytes used during our sampling program can be used in future investigations to develop more definitive conclusions regarding nitrate sources in Llagas Basin. Although such analytes as $\delta^{15}N$ have been used to identify nitrate sources in other studies, the lack of detailed hydrogeologic information and the lack of source and vadose zone sampling data currently preclude us from correlating our sampling results with specific nitrate sources. The $\delta^{15}N$ analysis is a way of measuring the ratio of the two isotopes ^{15}N and ^{14}N in the nitrate of a groundwater sample. This ratio depends on the reactions that formed the nitrogen compound and the isotopic composition of its source. Please refer to Rolston, et al, 1994a, Appendix 1, for a full discussion of the stable nitrogen isotope analysis. Despite limitations, a review of our nitrate and nitrogen isotope data indicates that fertilizer is the primary source of nitrates in groundwater in Llagas Basin. This finding supports the nitrogen loading data presented in our ``Nitrate Source Area Identification'' report.

The next phase of our study consists of the preparation of a Nitrate Management Plan. Information from this report as well as previous reports from this study will be used to develop the recommendations in that plan.

APPENDICES

APPENDIX A
REFERENCES

REFERENCES

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APPENDIX B
LABORATORY REPORTS—CHAIN OF CUSTODY FORMS